PRODUCTION OF CERIUM OXIDE MICROSPHERES BY AN INTERNAL GELATION SOL-GEL PROCESS

A Thesis

by

JEFFREY JOHN WEGENER

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

December 2008

Major Subject: Nuclear Engineering

PRODUCTION OF CERIUM OXIDE MICROSPHERES BY AN INTERNAL GELATION SOL-GEL PROCESS

A Thesis

by

JEFFREY JOHN WEGENER

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Approved by:

Chair of Committee,	Sean McDeavitt
Committee Members,	John Poston
	Miladin Radovic
Head of Department,	Raymond Juzaitis

December 2008

Major Subject: Nuclear Engineering

ABSTRACT

Production of Cerium Oxide Microspheres by an Internal Gelation Sol-Gel Process.

(December 2008)

Jeffrey John Wegener, B.S., Purdue University

Chair of Advisory Committee: Dr. Sean M. McDeavitt

The experiments performed for this research were completed to produce solid cerium oxide microspheres by an internal gelation sol-gel process. The motivation for this work was to develop a process that would enable the fabrication of a storage or transmutation form for the plutonium and transuranics (TRU) from the Uranium Extraction Plus (UREX+) used fuel reprocessing process. This process is being investigated by the Department of Energy (DOE) and the Advanced Fuel Cycles Initiative (AFCI) through the Nuclear Energy Research Initiative.

The internal gelation production of cerium oxide involves the combination of hexamethylenetetramine (HMTA), urea, and cerium nitrate solutions at ~100^{o}C. Microspheres were produced by injection of a broth solution into a flowing stream of hot silicone oil. The captured microspheres were aged, washed, and then underwent Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), and X-Ray Diffraction (XRD) analysis. The process variables examined in this study include the concentrations of HMTA, urea and cerium nitrate, the process temperature, the post-gelation aging time, and the product washing conditions.

Over a series of 70 experiments, it was determined that a broth solution containing a mixture of 1.45 M cerium nitrate and 1.65 M HMTA and urea (1:1 ratio) solutions produced the best cerium oxide microspheres. The spheres were aged for 30 to 60 minutes and then washed in hexane to remove the silicone oil and a subsequent series of ammonium hydroxide washes to remove unreacted product and to fully gel the microspheres.

Through DSC analysis it was determined that excess wash or unreacted product may be removed by an exothermic reaction at approximately 200^{o}C. The XRD analysis of unheated spheres showed the presence of cerium oxide with additional cerium-bearing organics. Following heating, the microspheres were completely converted to cerium oxide.

DEDICATION

This thesis is dedicated to my parents John and Susan Wegener, my brother Michael Wegener, and my sister Sarah Wegener.

ACKNOWLEDGEMENTS

I would like to thank my committee chair, Dr. Sean McDeavitt, for his support and the opportunity to study at Texas A&M University. I would also like to thank my committee members, Dr. John Poston and Dr. Miladin Radovic, for their assistance. Thanks go to Zane Adams, Michael Naramore, and Jeffrey Hausaman for assisting in the analysis work, and to Luis Ortega, Adam Parkison, and Aaron Totemeier for their encouragement and advice along the way. Finally, I would like to thank my family for everything along the way, big and small, that has made this possible.

NOMENCLATURE

AFCI	Advanced Fuel Cycle Initiative
DSC	Differential Scanning Calorimetry
DOE	Department of Energy
HMTA	Hexamethylenetetramine
MOX	Mixed Oxide
NERI	Nuclear Energy Research Initiative
ORNL	Oak Ridge National Laboratory
PUREX	Plutonium and Uranium Extraction
RTV	Room Temperature Vulcanizing
TGA	Thermogravimetric Analysis
TRISO	Tristructural-Isotropic
TRU	Transuranic
TRUEX	Transuranic Extraction
UREX	Uranium Extraction
XRD	X-Ray Diffraction

TABLE OF CONTENTS

Page

LIST OF FIGURES

Page

LIST OF TABLES

1. INTRODUCTION

Presently in the United States, used nuclear fuel is accumulating at power plants at a rate of ~2,000 metric tons per year. As of 2007, over 55,000 metric tons were awaiting long term disposal in used fuel storage pools and dry casks [1]. The amount of recoverable energy stored in this volume of used fuel is extraordinary when compared to other long term energy options. To produce 8000 kWh from coal would require 3 metric tons of high quality black coal. This much coal would produce 8 metric tons of carbon dioxide and up to 100 kg of sulfur dioxide. The same amount of energy can be produced from between 30 and 70 kg of natural uranium, or about 30 grams of enriched fuel [2]. Assuming an enrichment of 1% on used nuclear fuel, the same energy load could be obtained from 21 to 49 kg.

The United States Department of Energy is exploring two different pathways to address the issue of this accumulating nuclear waste. The first option is long term storage at a repository. Yucca Mountain, located approximately 90 miles from Las Vegas, has been designated as the site for the long term repository. Under this plan, as outlined in the recently filed license application, 63,000 metric tons of used fuel from commercial reactor sites would be deposited in tunnels within the mountain [3]. Given current generation rates, in less than a decade more commercial used fuel would have been produced than the capacity of Yucca Mountain can accommodate. Using only repositories to store the waste, by the end of the current century several more deep

---

This thesis follows the style of Journal of Nuclear Materials.

geologic storage facilities would be required.

The second option being investigated would attempt to avoid long term storage by reprocessing and recycling used nuclear fuel. Under this pathway, the 8 to 11 kg of U-235 present in one metric ton of used fuel will be put back into service along with the useful energy content retrievable from plutonium and other transuranics. Two processing options are being put forward to accomplish the recycling process and produce usable fuel [1]. The first option, Plutonium and Uranium Recovery by Extraction (PUREX), separates high purity uranium and plutonium from the waste stream. PUREX is used worldwide for fuel reprocessing and the production of weapons grade fissile materials. The second recycling option, which is currently being promulgated by the US Department of Energy, is a modified PUREX process designed to eliminate pure plutonium extraction. This process is named UREX (Uranium Extraction) and it has the potential to save space inside a repository site such as Yucca Mountain by removing the uranium which makes up the vast majority of the mass of used fuel as well as some of the more active fission products. By utilizing UREX, the plutonium remains in the raffinate, or waste, stream with the other transuranics (TRU) and fission products, mitigating the proliferation issue. It will take a social policy decision to determine whether these Pu and TRU isotopes will be stored as waste or burned as fuel, but the research described here will support either mission.

The US Department of Energy is developing UREX and associated processes under the Advanced Fuel Cycle Initiative. One of the mechanisms used to advance this technology with university research is the Nuclear Energy Research Initiative (NERI).

The research presented in this thesis represents a portion of the larger NERI project designed to investigate the ultimate disposition form for the plutonium and TRU isotopes from the raffinate stream A complete family of separation processes, referred to as UREX+, have been designed to perform multiple operations to selectively isolate specific isotopes for individual treatment. The effluent stream containing the PU/TRU nitrate effluent comes from the TRUEX (TRU Extraction) process at the tail end of the UREX 1a scenario.

The focus of this project is on the development of a conversion process to transform mixed uranium and Pu/TRU nitrate solutions into solid mixed oxide microspheres. The results demonstrate the preliminary process methodology using cerium nitrate as a surrogate for plutonium nitrate. The overall NERI context for this cerium nitrate conversion process is a larger project designed to develop a comprehensive conversion scheme involving three processes: 1) the conversion of the U/Pu/TRU nitrates to oxide powder, 2) the recovery of a portion of the spent Zircaloy cladding as a metal powder via a hydride/dehydride process, and 3) the fabrication of cermet pins by combining both powders via hot extrusion. The final cermet is a candidate storage form that may also serve as a TRU-burning inert matrix fuel. The Zircaloy recovery and hot extrusion processes have been developed as separate projects [4, 5, 6, 7]. In addition to these process development activities, computational simulations evaluating the Pu and TRU-burning potential of this extruded fuel form in advanced reactors are being performed at Purdue University and the University of California, Berkeley [7].

As the first process development stage for nitrate conversion, an internal gelation sol-gel system was created based on the conversion of cerium nitrate. In this method, a "broth" containing the nitrate solution, urea, and hexamethylenetetramine (HMTA) was injected into a hot flowing stream of silicone oil. Through the temperature driven sol-gel process, solid microspheres were produced, washed, and sintered for evaluation. This conversion process is similar to that used in the fabrication of UO_2 tristructural-isotropic (TRISO) fuel kernels for pebble bed and prismatic nuclear reactor systems [8]. Since the UO_2 process is well developed, this research focused on the gelation of cerium oxide as a first step toward the gelation of mixed uranium-cerium oxide microspheres.

The design of the sol-gel apparatus and the baseline processing data generated by this research will serve as a foundation for further work into mixed oxide microsphere gelation. A sequence of seventy internal gelation experiments were completed. The initial testes were used to identify appropriate processing variables and multiple system modifications were required as the process was developed. Through a set of parametric studies, it was discovered that the highest quality cerium oxide spheres were produced from a broth of 1.45 M cerium nitrate and 1.65 M HMTA and urea. Spheres produced from this broth composition were fully washed in hexane and underwent a series of ammonium hydroxide washes. These washed and dried spheres underwent varying levels of heat treatment and were then analyzed through x-ray diffraction (XRD), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). The final sintered microspheres were clearly identified as cerium oxide, whereas the freshly gelled and washed spheres were comprised of cerium oxide along with a remnant of

organic impurity compounds. The following Sections describe the theoretical basis (Sections 2), experimental design (Section 3), experimental results (Section 4), and discussion (Section 5) from the research that created this conclusion.

2. PREVIOUS WORK

2.1. Sol-Gel Processing of Metal Oxide Ceramics

The name “sol-gel” refers to a family of liquid-to-solid conversion processes that produce solid materials from an initial chemical solution. The name itself is a reference to the starting solution, or “sol”, and the solid material produced from the “gelling” of inorganic polymers that form networks to produce a solid. In the case described here, the solid being produced is cerium oxide and the method is based on a sol-gel process developed for uranium dioxide fabrications.

There are two sol-gel process types that are used extensively in materials processing applications: external gelation and internal gelation. In both cases, the sol-gel reaction is driven by the presence of ammonia (NH_3). For external gelation, an external solution of ammonia is used to drive the gel-forming reaction [9]. However, external gelation is not practical for the production of microspheres because it would require many gallons of ammonia to be used as a heat transfer medium and a host for the reactant droplets that gel during the process. Therefore, internal gelation is commonly used to produce powders. For internal gelation, the required ammonia is produced internally by the decomposition of HMTA [9]. Internal gelation was used for this project and the basis for the experimental method is described in the next section.

2.2 Chemistry of UO_2 Internal Gelation

As stated above, the internal gelation sol-gel process involves the reaction of a nitrate salt with ammonia to produce a spherical gel and the ammonia is produced

internally by the decomposition of HMTA [9]. The discussion in this section outlines the sol-gel process designed for UO_2 TRISO kernels, as developed by Oak Ridge National Laboratory [9].

The starting uranyl nitrate is prepared as an aqueous solution (in contrast, cerium nitrate is used to generate cerium oxide spheres). The active chemical reagents for UO_2 internal gelation are the uranyl nitrate salt combined with urea ($(NH_2)_2CO$) and HMTA ($(CH_2)_6N_4$) inside of an inert heat transfer medium, such as silicone oil. The combination of the nitrate, urea, and HMTA is commonly referred to as the "broth" [9]. Before this broth can be used to produce microspheres, it first must be chilled to approximately 0°C. By doing this, urea combines with the nitrate salt to stabilize the solution and prevent early gelation [10]. This stabilizing reaction is given as equation 1.

$$UO_2\left(NO_3\right)_2 + 2(NH_2)_2CO \rightleftharpoons UO_2(NO_3)_2 \cdot 2(NH_2)_2CO \quad (1)$$

After the broth is stabilized, the temperature is increased by introduction of the broth into the silicone oil at 90 to 110°C, the urea decomplexes and the above reaction is driven to the left. When the broth introduction is accomplished using a small needle, the liquid forms spherical droplets in the silicone oil. The reaction sequence that follows takes place within the spherical solution. First, the nitrate salt loses its nitrate group and undergoes hydrolysis [10], as shown in Equation 2.

$$UO_2^{2+} + 2H_2O \rightleftharpoons UO_2(OH)_2 + 2H^+ \quad (2)$$

At this point, all species are still soluble and the hydrogen ions produced by the hydrolysis reaction then undergo a protonation reaction with the HMTA [10], as shown in Equation 3.

$$(CH_2)_6N_4 + H^+ \rightleftharpoons (CH_2)_6N_4 \cdot H^+ \quad (3)$$

Protonation of the HMTA continues until at least 95% of the HMTA molecules have picked up an extra hydrogen ion. At this point the decomposition reaction will occur reducing the protonated HMTA to ammonium and formaldehyde [11], as shown in Equation 4.

$$(CH_2)_6N_4 \cdot H^+ + 3H^+ + 6H_2O \rightleftharpoons 4NH_4^+ + 6CH_2O \quad (4)$$

All species are still soluble at this point.

The urea ($(NH_2)_2CO$) that had originally complexed with the nitrate salt at 0°C according to equation 1 and then decomplexed back into solution at ~100°C now has a second role to play in the reaction sequence. Urea and formaldehyde readily react together to produce monomethylol urea [10]. As this goes on, the reaction in Equation 4 is driven completely to the right as the formaldehyde product is consumed as fast as it is produced and the reactants strive for equilibrium.

Once the ammonium is produced, the final product is precipitated as a solid. This occurs as a rigid gel structure of hydrated uranium oxide with ammonia (a solid at 100°C) is formed by the cross linking of weakly bonded particles [12]. Since the reaction sequence transpires within the spherical solution droplet suspended in the silicone oil, the final product is a solid sphere. The sphere forms rapidly, but the

reaction needs time to go to completion, so the spheres are "aged" in the hot oil to ensure completeness.

2.3 Microsphere Production for TRISO Fuel Kernels

In the past several years, several research teams have investigated the production of microspheres by internal gelation sol-gel. The research team at Oak Ridge National Laboratory produced microspheres of 1200, 300, and 30 μm and they investigated the details for most of the steps in the gelation process described above. For all but the fine spheres, trichloroethylene was used as the gelation medium with temperatures ranging from 54 to 64^{o}C. The height of the gelation column in these experiments was 180 cm, allowing for a slower heat transfer rate. The broth for these sets of experiments consisted of a 1.3 M uranium solution and an HMTA / uranium and urea / uranium mole ratio of 1.25. After removal of the organic medium, the produced spheres were washed in a solution of 50% isopropyl alcohol and 50% 1.5 M NH_4OH. The next wash was a 0.5 M solution of NH_4OH. The final wash was 75% isopropyl alcohol and 25% water. Each of these washes was for 45 to 70 minutes. Drying of the spheres was accomplished by flow of air over the spheres. The first step in the sintering process involved placing the spheres into a flowing stream of argon – 4% hydrogen increasing in temperature to 450^{o}C for one hour. Finally they are loaded into molybdenum trays and rapidly heated to 1600 ^{o}C for four hours, then allowed to cool. The spheres produced had upwards of 99% theoretical density, were 88.2 weight percent uranium and had an oxygen to uranium ratio of 1.98 to 2.0 [13].

Other work at Oak Ridge was completed to produce 500 µm for use as TRISO fuel kernels [14]. This setup used a vibrating needle to deliver the broth into a veil of falling oil. The height of the gelation column used was 550 mm with a flowing oil temperature of 60°C. Stock solutions of 2.7 M acid deficient uranyl nitrate were produced. Acid deficient refers to the ratio of NO_3^- to U. The lower this number, the more acid deficient the solution is. The final broth solution had an HMTA and urea ratio to uranium of 1.3. After production of spheres, they were allowed to age in the silicone oil for up to 30 minutes then washed in four solutions of trichloroethylene for a minimum of 15 minutes per wash to remove the silicone oil. The next series of washes was 30 minutes of 0.5 M NH_4OH until the electrical conductivity was below 800 µmhos; the spheres are then allowed to air dry. Sintering of the spheres was carried out in either a pure nitrogen or 5% hydrogen – argon environment. The heating profile was 80°C for two hours, 150°C for three hours, 600°C for five hours, and finally 1550°C for five hours [14].

Subsequent research at Oak Ridge was completed to produce both 350 and 500 µm spheres [8]. The broth for this series of experiments has been optimized to work for a wider range of sphere sizes. Uranium concentration within the broth is between 1.29 and 1.30 M, HMTA and urea are both 1.68 M, and NO_3^- is 2.00 to 2.08 depending on the acid deficiency of the uranyl nitrate. The sintering of the spheres is the same as above except a 4% hydrogen – argon flow was used at approximately 3 L per minute. During sintering, the spheres shrink from their original size. Dried spheres of 1000 µm in size

were observed to shrink to between 500 and 532 µm after sintering, shown in Figure 1 [8].

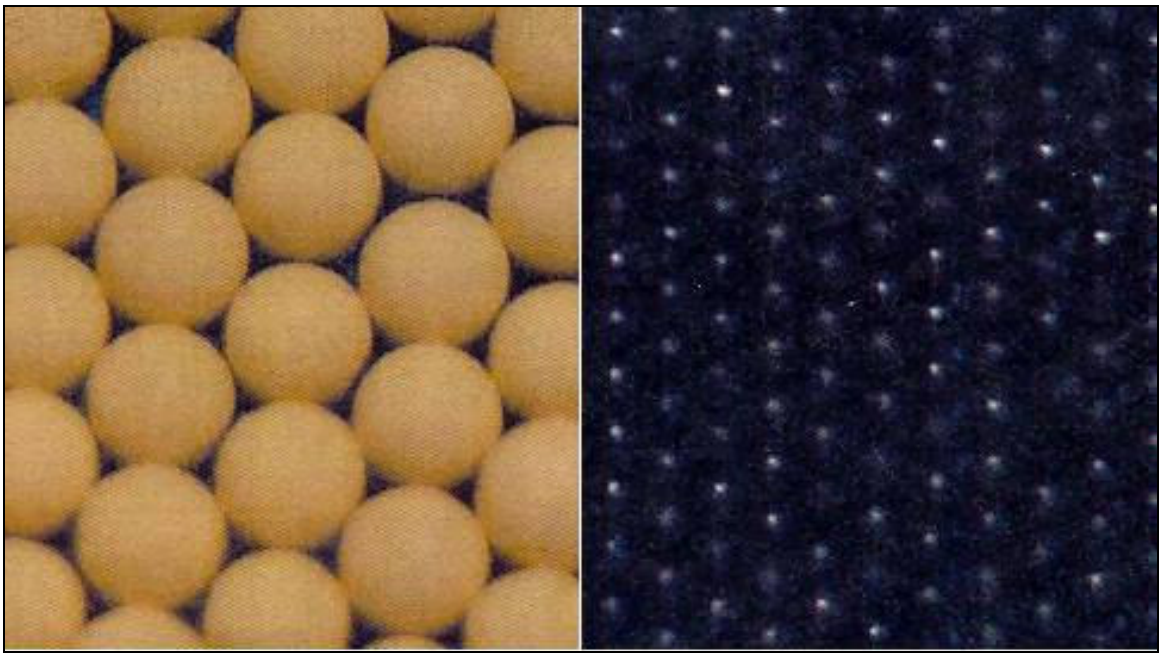

Figure 1. Dried UO_2 spheres (~1000 µm diameter, left) and sintered UO_2 spheres (500 to 532 µm diameter, right) [8].

Two main injection methods have been used in the creation of oxide microspheres. The first involves the spheres flowing through a vibratory nozzle into a veil of silicone oil. The second method involves directly inserting a needle into the flowing oil. One of the systems at Oak Ridge employed this latter setup [15] and a schematic is shown in Figure 2. Oil was heated in a reservoir where the collection basket was also located. From the reservoir, a pump drew the oil through the system where it went into the sphere-forming column from both the top and bottom. The broth was injected into the oil upstream of the column using a forced air injection method.

After forming in the column, the spheres were carried through a section of tubing back into the reservoir [15].

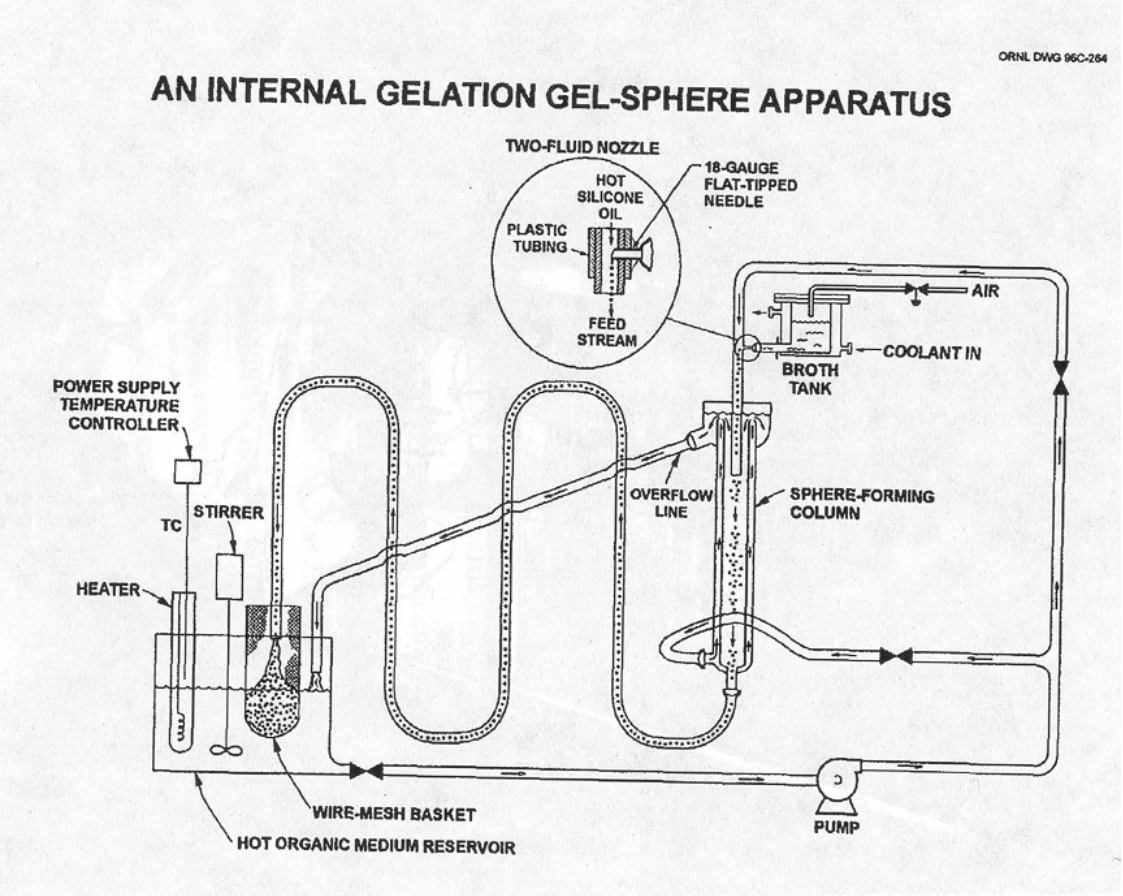

Figure 2. Diagram of Oak Ridge internal gelation sol-gel system [15].

While the work described previously focuses on UO_2 microsphere production, many oxide materials may be formed by sol-gel. For the presented research, cerium is used as a surrogate for plutonium. Cerium is able to be used due to the physical similarities between cerium oxide and plutonium oxide in a batch handling and compaction manner. The similarities also extend to the sintering process, where the two oxides exhibit nearly identical shrinkage behavior [16].

3. EXPERIMENTAL DESIGN AND PROCEDURE

The experimental sol-gel apparatus created for this project was based on the system used at Oak Ridge National Laboratory (Fig 2) [15] with custom modifications made as the experimental experience was gained. Figure 3 shows a schematic diagram of the final configuration of this device (used for experiments 17 through 70) and Figure 4 is a photograph of the installed apparatus.

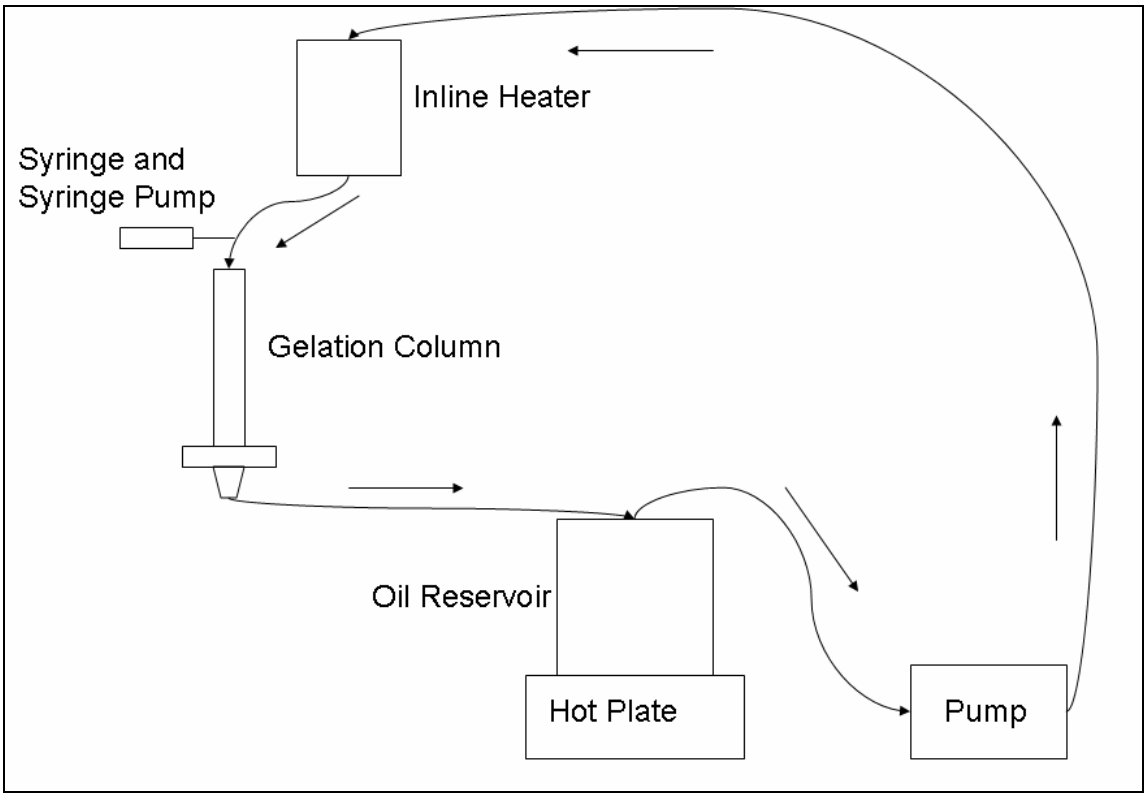

Figure 3. Schematic diagram of the final experiment configuration.

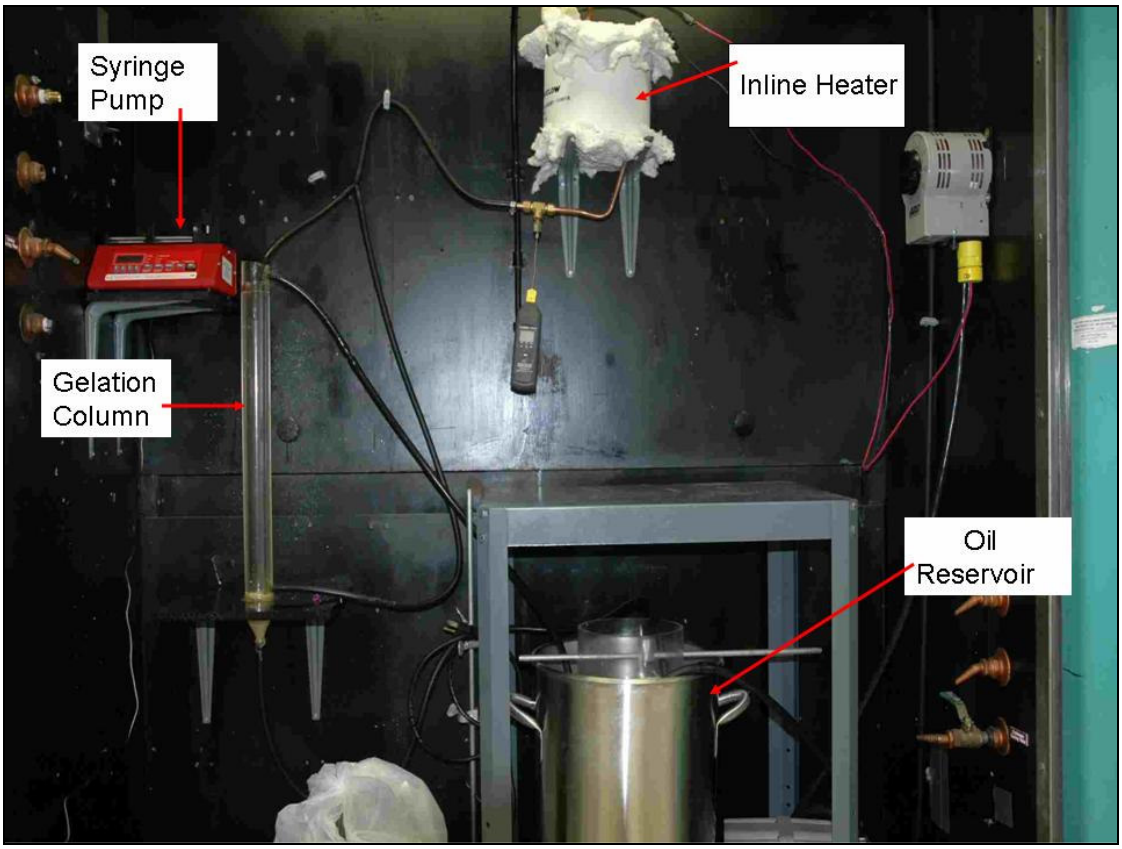

Figure 4. Photograph of the final experiment configuration.

In this system, an oil reservoir is heated by a hot plate, drawn through the system by a peristaltic pump, and the temperature of the flowing oil is then controlled to the desired operating temperature (nominally an experimental variable set near ~100^{o}C) while passing through a copper coil inside of an inline ceramic fiber heater. The precursor mixture of reactants, or the broth, is injected into the system using a syringe pump that is located directly upstream of the gelation chamber. The chemical consumption of the broth begins immediately upon insertion into the warm oil. The oil is an inert host to the gelation process and serves to provide heat and to carry the gelled

spheres to the catch basket at the end of the flowpath. Once the oil passes through the gelation chamber and into the catch basket it flows back into the reservoir.

3.1 Experimental Design

3.1.1 Oil Heating and Delivery

The silicone oil used in the system is stored in the oil reservoir. This reservoir is a 6 gallon stainless steel batch can. This reservoir is a seamless stainless steel pan that prevents oil from escaping the system, even when heated. Providing heat to the reservoir is a Thermolyne Type 2200 Hot Plate. The oil in the reservoir and microspheres present during aging are maintained at 90 to 100^{o}C by the hot plate heater.

The hot oil is pumped through the system by an Anko Mityflex peristaltic pump. The pump operates by placing the rubber tubing within the pump housing where three rollers force the oil through the tubing driving it through the rest of the system. The tubing is inserted into the reservoir on one end and sent to the gelation chamber on the other. By driving the oil through the system in this way, no part of the pump is contaminated by anything present within the oil. This is especially necessary for the future work where uranium gelation may be performed. Precautions must be taken to ensure that the section of tubing present in the pump housing does not become worn.

The hot plate is able to heat the oil to the correct temperature near 100^{o}C, but it is not able to give fine control over the oil that is flowing through the system. After pumping, it was observed that the oil was cooling in the line and needed a second heater to control the oil temperature prior to its entrance to the gelation chamber. Therefore, a Watlow 1100 W ceramic heater with an internal copper coil was installed between the

pump and the gelation chamber. Within the heater, a section of copper tubing has been coiled to provide a longer flow path inside of the furnace and to enable better heat transfer and higher temperatures than are achievable with rubber tubing.

3.1.2 Broth Delivery and Gelation

The initial method used to deliver the cerium-loaded broth into the gelation chamber was a pressurized broth pot and a forced air system. The broth pot was constructed using a section of acrylic tubing with a ball valve at the bottom to allow flow to the injection needle. At the top of the cylinder was a Swagelok tube fitting allowing connection to the air system. This was based on the setup observed at Oak Ridge National Laboratory for TRISO fuel kernel gelation.

Several variations of the forced air system were considered before the concept was abandoned altogether. The first involved a direct line from the building air supply into the broth chamber; although this was soon discovered to be far too much pressure. The next step involved several different pressure regulators, with the most time spent using a Control Air Inc. Type 700 Pressure Regulator in conjunction with a 15 psi pressure gauge. The whole broth pot system and forced air system was scrapped when it was discovered that the injection rate required for success was much lower than could be provided by any of the regulators (in other words, the insertion was too fast and difficult to control).

The final injection system installed on this system, and the method used for most of the experiments, involves a 5mL syringe and a New Era NE-300 syringe pump. In this method the syringe is loaded with the broth then placed into the syringe pump. The needle from the syringe is placed in the flowing oil, the desired injection rate is set, and then the dispense button is pressed. Flow rates were on the order of 0.2 – 0.3 mL/min; much below what any of the air pressure regulators could provide.

The volume of the system where the gelation occurs is referred to as the gelation column and a schematic of this setup is shown in Figure 5. It was constructed using two differing diameters of acrylic tubing, an ABS plastic sheet, and a funnel. The outer, larger tube is slightly higher to allow an overflow spout for the oil. This tube is then secured to the plastic sheet at the bottom. The inner tube is connected to nothing at the top and is sealed onto the funnel at the bottom using epoxy. The top of the funnel is secured to the bottom of the plastic sheet. A photo of the final setup is shown in Figure 6.

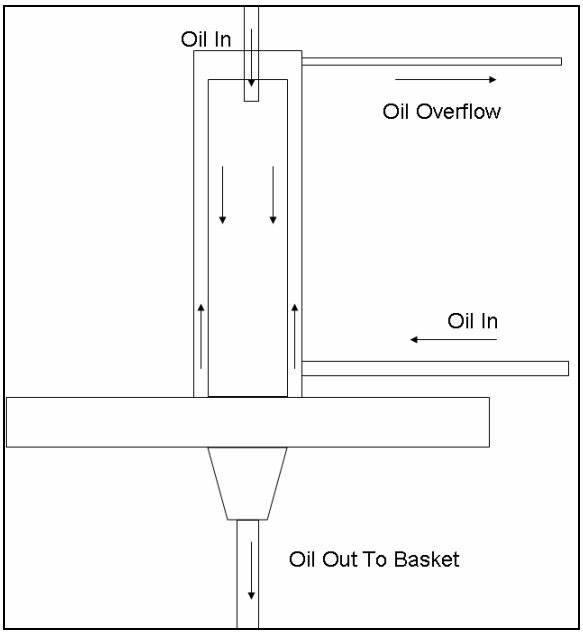

Figure 5. Schematic diagram of the gelation column

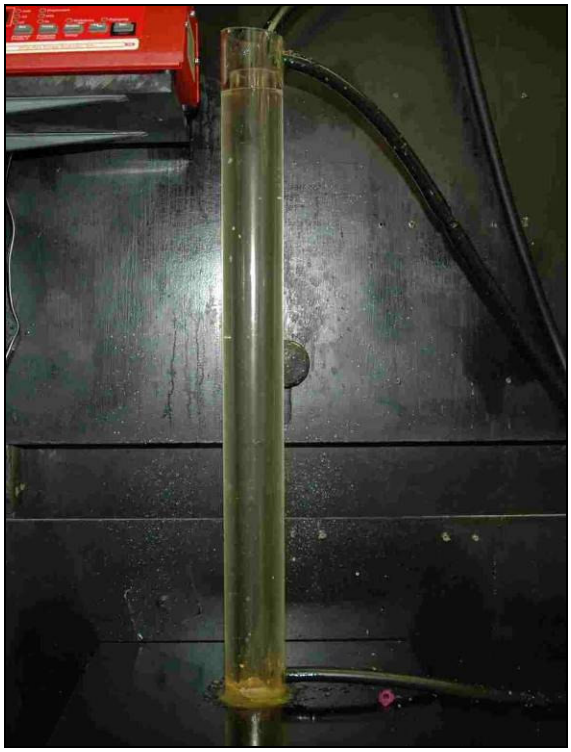

Figure 6. Photograph of the installed gelation column.

Once the oil leaves the gelation column it flows back into the oil reservoir where all gelation products are collected in the catch basket. Three types of mesh basket were used in the experiments, as described in Section 4. The first type of catch basket was constructed using sheets of woven stainless steel wire mesh (250 by 250 wires per inch). Using a 12" x 24" sheet of mesh, a cylinder was made approximately 5.75" in diameter. To one end of the cylinder a circle of the same mesh was attached using Room Temperature Vulcanized (RTV) Silicone Sealant. The second basket model used 80 x 80 mesh woven stainless steel wire. The final basket model was constructed using 40 x 40 mesh stainless steel wire. The courser mesh is better for post gelation washing since the washing fluids must drain through the mesh, allowing all washing steps to be performed with the sol-gel spheres in the constructed baskets rather than removing them spheres from the basket. In all cases, the mesh collection baskets were placed inside of the oil reservoir using an open acrylic cylinder to suspend it above the reservoir oil level. The acrylic cylinder has drain holes on the sides and a sheet of the wire mesh across the bottom to allow for drainage and filtration. This entire system (basket and acrylic cylinder) is then suspended in the reservoir such that the basket is above the oil and the cylinder does not touch the floor of the reservoir.

3.2 Experimental Procedure

The procedure described here represents the final procedure developed during the experiments described in Section 4. In a way, this procedure is a result of the research, but it is included in this section to provide understanding of how the experiments were performed. Variations from this procedure are described throughout Section 4,

especially for the earlier experiments. In the final experiment, solid microspheres were produced using this method.

The first step in running an internal gelation experiment is to prepare stock solutions of the primary broth constituents. The two reactants are kept apart to prevent gelation from occurring during storage. The first solution contains 3.0 M cerium nitrate, and the second solution is a mixture of both HMTA and urea (3.2 M for each). To create a stock solution containing HMTA and urea, the solid form of each compound is dissolved in deionized water and brought to the desired volume and molarity. The two solutions are both stored at room temperature as they are stable at that point. The experimental solutions used in the tests described in Section 4 were all diluted from these stock solutions to the experiment-specific desired concentrations.

For an experiment run, the first step is to turn on the hot plate under the oil reservoir. Doing this first allows a majority of the oil to heat when the system does not need to be attended. Typically the hot plate is set to 125^{o}C. While the oil is heating, the broth to be used in the run can be prepared. Calculated amounts from the stock 3.2 M HMTA/Urea and 3.0 M cerium nitrate solutions are measured corresponding to the desired concentrations of each in the run to be performed. To accurately measure out the solutions, 2 mL pipettes and a pipette pump are used. Each of the solutions were measured into test tubes and placed into a freezer for an hour to adequately chill them. At the beginning of each experiment the two solutions are combined together, stirred thoroughly, and then placed back into the freezer until it is time for the run to begin. This allows the urea to complex with the nitrate according to the reaction in Equation 1.

When the oil has heated sufficiently, the peristaltic pump and the ceramic fiber heater are turned on. The heater is powered through a variac and is generally needed to be at approximately 50% power to heat the oil passing through the system to approximately 100^{o}C. Constant attention needs to be paid to the system when the pump is in operation so that the oil does not overflow the gelation column. For this reason it is typically turned to the lowest level possible setting to bring the oil up to the overflow weir located near the top of the column. Once the oil heats and its viscosity decreases, it flows faster through the column and the speed of the pump can be adjusted. For an experiment run, the pump is set to 30%.

The last step before performing an experiment run is to prepare the broth solution and syringe. The syringe is readied by removing it from the freezer and attaching the desired needle (the needle gauge size is an experimental variable). Having the syringe chilled helps in the prevention of premature gelation of the broth in the syringe and needle. The broth from the freezer is loaded into the syringe, air is removed from the syringe by plunging until broth is released, and then the system is placed into the syringe pump and secured. The final pre-experiment step is to insert the needle into the oil stream by either piercing the tubing or placing it into a pre-existing hole. Once everything is secure and ready the syringe pump is started and the broth is injected into the oil stream.

After the desired amount of broth has been injected into the system the syringe pump is stopped and the syringe and needle are removed from the pump. The spheres that have been formed must remain in the catch basket for an additional amount of time

for the gelation process to be completed. This step is called aging. During this time the heaters and peristaltic pump remain on to keep hot oil flowing through the system and over the gelling spheres.

When the aging process is complete, the catch basket is removed and placed into the wash basin. The spheres are first washed with hexane to remove the silicone oil. The next series of three washes are designed to remove any reaction products still on the microspheres and to provide ammonium hydroxide to allow further gelation for improved sphere properties [13].

The three washes in the main process are each for 60 to 75 minutes and 200 mL of wash solution for each. First in the process is a solution of 50% isopropyl alcohol and 50% 1.5M Ammonium Hydroxide. The second primary wash involves a solution containing only 0.5M Ammonium Hydroxide. The final wash step is 75% isopropyl alcohol in water [13]. Once this has been completed the spheres are removed from the catch basket and placed aside to dry. After drying is completed, the spheres ready for sintering and further characterization. As evidenced by the results in Section 4, this washing procedure is a critical component of the production of the final microspheres.

4. RESULTS

A series of 70 experiments was performed using the apparatus and procedures described in Section 3. The experimental apparatus underwent several changes in design to address issues that arose as the research progressed. Throughout the series of experiments, equipment was replaced, added, and removed in the quest to produce solid, reproducible microspheres. Major system additions involve the removal of the forced air system and broth chamber, addition of the gelation column and syringe pump, and replacement of the oil reservoir system (each of these items are described in Section 3). Additionally, since the majority of literature on this subject deals with uranium oxide (U_3O_8 and UO_2) microsphere production, additional experiments were required to evaluate the impact of changes in chemical composition of the broth.

Figure 7 shows a chronological flowchart of the experiments performed for this project. The experiments are divided into three stages of development: 1) system development experiments (Section 4.1), 2) process development experiments (Section 4.2), and 3) microsphere production and characterization (Section 4.3).

Experiment 1 (Section 4.1.1) was an initial trial run using several equipment items that are no longer part of the system. In experiments 2 through 12 (Section 4.1.2) the broth chamber and flow regulator were replaced and the gelation column was added. Section 4.2.1 reports a series of small scale process development tests completed in test tubes to evaluate the optimum broth composition for sphere production. In experiments 13 to 16 (Section 4.1.3) the forced air system was removed and a manual injection via

syringe was used. In experiments 17 and 18 (Section 4.1.4) a syringe pump replaced manual injection. Experiments 19 to 36 (Section 4.2.2) explored variation in the broth composition and experiments 37 to 48 (Section 4.2.3) continued this process while also changing the catch basket designs. Experiment 49 through 53 (Section 4.2.4) continue with the evaluation of the broth concentrations, but a three-stage wash system developed at Oak Ridge National Laboratory was also implemented [7]. Experiments 54 to 59 (Section 4.2.5) used the same fixed broth composition with varying aging times, and Experiments 60 through 66 (Section 4.2.6) used diluted solution in an effort to obtain quality washed spheres. The final experiments performed, 67 through 70 (Section 4.3.1), focus on the final broth composition while exploring variations in the temperature of the silicone oil and the times for aging and washing. The X-Ray Diffraction (XRD), Thermogravimetric Analysis (TGA), and Differential Scanning Calorimetry (DSC) analyses (Section 4.3.2) were performed to characterize the product and evaluate the post-washing sintering of the microspheres.

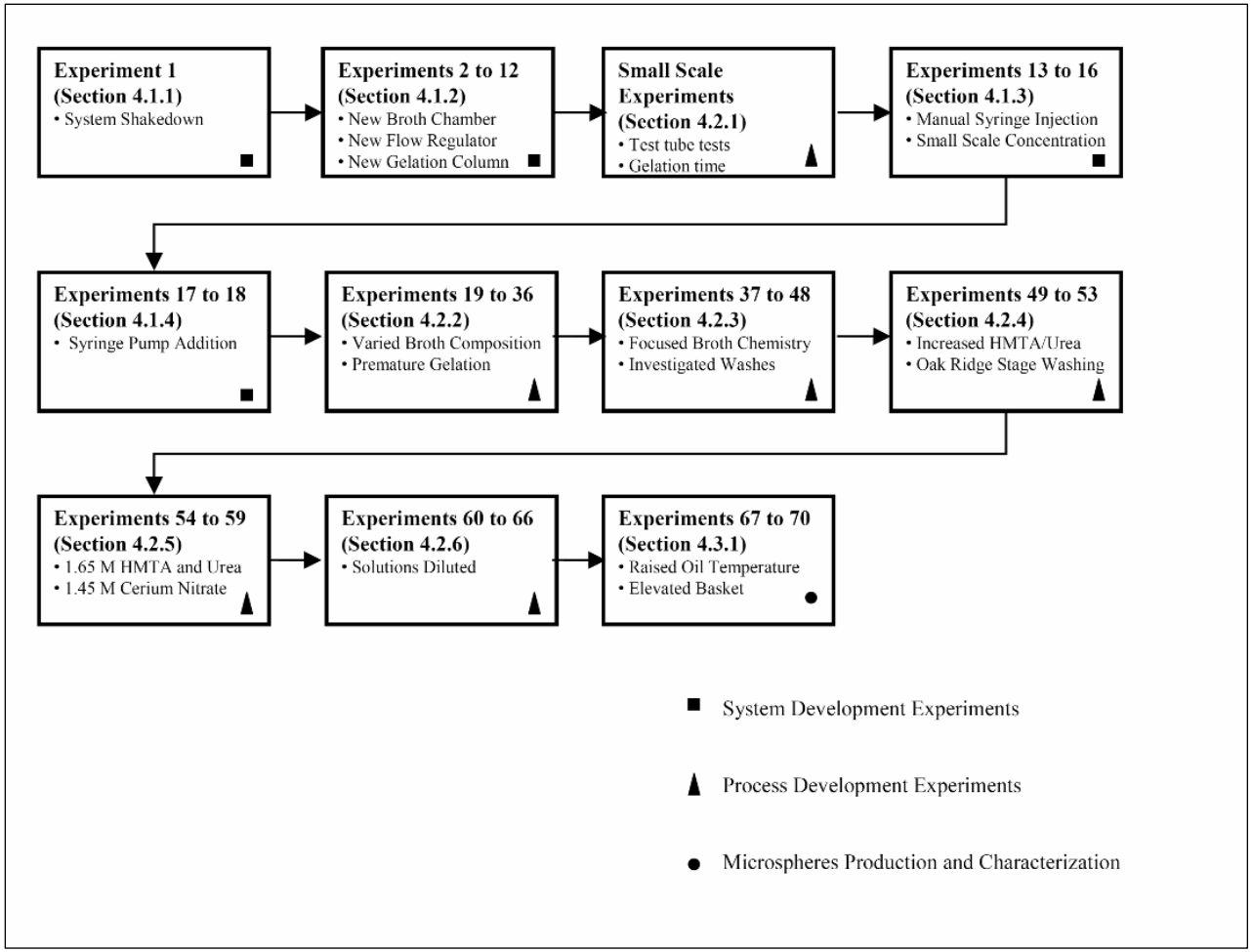

Figure 7. Chronological flowsheet of system and process experiments.

4.1 System Development Experiments

Experiments 1 to 18 were all performed to gain understanding of microsphere production and to establish the proper system components to enable that production. Throughout these tests, the sol-gel system evolved and the equipment changes mentioned in Section 3 were implemented as systematic flaws were discovered or to simplify operations.

4.1.1 System Shakedown (Exp. 1)

The first experiment used an experimental apparatus that only slightly resembles the system used in later runs. The oil reservoir was a steel pan suspended in a NesLab constant temperature bath. A glass separatory funnel was used as the broth chamber with forced air provided by a gas tank regulator. The microsphere catch basket was a sheet of stainless steel mesh (250 x 250 wires per inch) folded into a funnel shape that was placed over the steel pan reservoir.

For this experiment the constant temperature bath was set to 110^{o}C and the oil flowing through the system was maintained at 90^{o}C. The broth composition was 1.3 M cerium nitrate, 1.68 M HMTA, and 1.68 M urea and the total broth volume was 75 mL. The solutions of HMTA/urea and cerium nitrate were kept separate and chilled in an ice bath while the oil in the system was rising in temperature; before being poured into the broth chamber, the solutions were combined and stirred.

When the 18 gauge needle (0.838 mm inner diameter) was inserted into the tubing and the stopcock opened, no broth was initially injected into the system so the pressure on the regulator was increased until injection occurred. After a short time, a

gelled substance began to form in the mesh funnel that eventually began to limit drainage flow. To counter this, the speed of the pump was manually adjusted until all of the broth had been injected and drainage flow was stabilized in the funnel. After 10 minutes of aging it was noted a gel surface had also formed on the bottom of the oil reservoir. After an hour of aging, the material in the funnel never fully gelled and a solid yellow crust formed on the bottom of the reservoir.

4.1.2 System Modification Tests (Exp. 2 to 12)

Several system changes were made after experiment 1. The first change made was the replacement of the oil reservoir and redesign of the catch basket. The second change involved replacing the broth chamber and air pressure regulator. Finally, the gelation column was added to allow a volume of slow, non-turbulent flow for the broth droplets to flow through while undergoing the gelation process.

Experiment 2 used the same broth composition, volume, and flowing oil temperature as experiment 1. Initially, a pressure of 4 psi was used to inject the broth but this was increased to 4.5 psi as broth was not flowing out of the broth chamber. Once this pressure was reached the broth was forced out too quickly and produced a result that initially looked similar to experiment 1. Examining the product after it was allowed to age and dry showed that it maintained its globular form rather than being a powder. Experiment 3 netted a product similar to experiment 2 using an injection pressure of 3.75 psi before the needle became clogged; a representative photo of the product is presented in Figure 8.

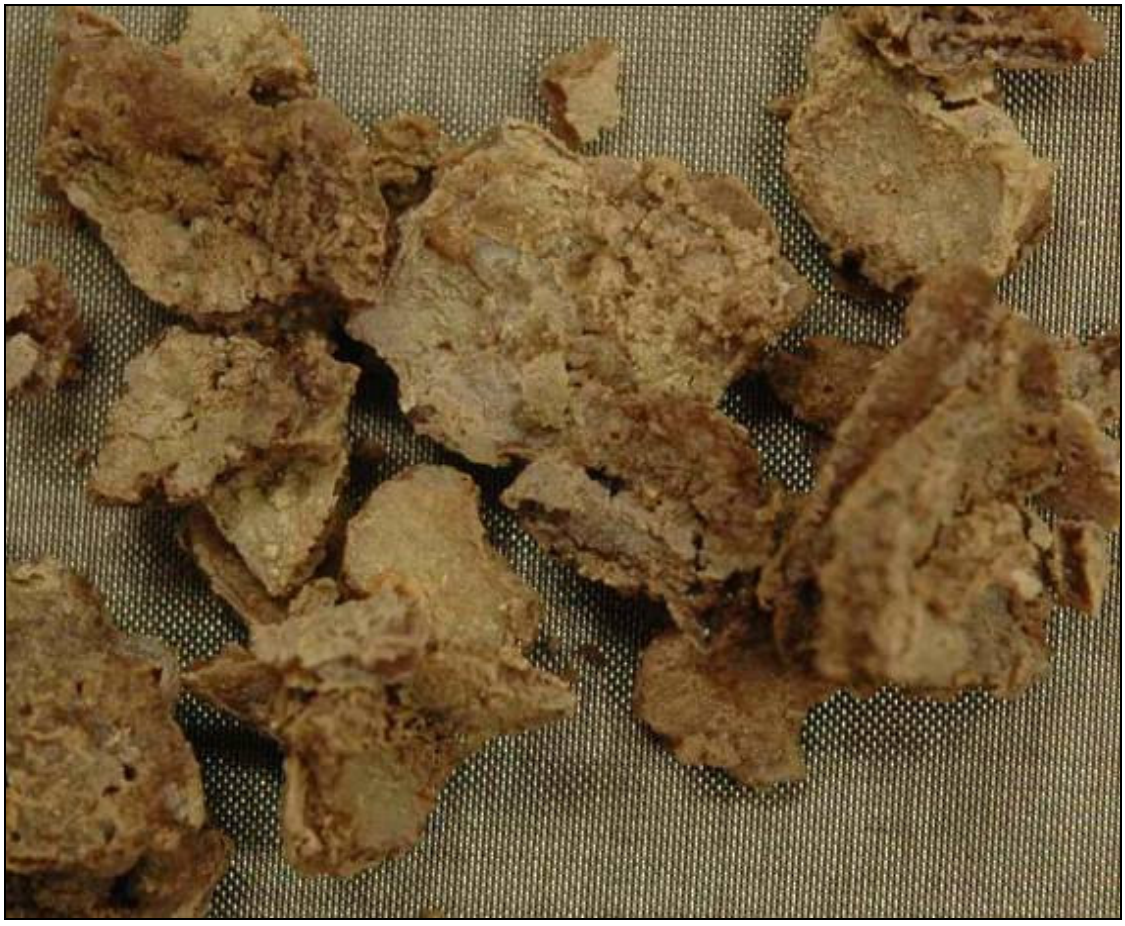

Figure 8. Photograph of product obtained from experiment 3.

For experiment 4 a system was developed to keep the broth chilled up to the point of injection in an attempt to overcome the clogged needle that had occurred in experiment 3. The same chemistry was used with an initial pressure of 3.75 psi that was increased to 4 psi until the nozzle on the broth chamber became clogged preventing any air from forcing broth into the system. Before clogging occurred, small white flecks were observed flowing from the output hose into the catch basket. After drying, these flecks were observed to be several gel spheres of varying size. Experiment 5 produced

nearly identical results of white specks in the output stream before the flow was clogged. It appeared, on inspection of the broth delivery system, that the broth was frozen around the metallic parts in the system. This prompted the replacement of the metal ball valve and nozzle with plastic.

For experiment 6, the injection ice bath was removed to prevent broth freezing. Before the needle was inserted into the oil line, the ball valve was opened to initiate flow before insertion to allow the broth to be flowing out of the needle as it is inserted into the tubing. A pressure of 4 psi was used initially, although this was determined to be too high as a mixture of gel globs and spheres were produced. Experiment 7 used the same conditions as 6, but with an injection pressure of 3.75 psi that enabled slow-flowing broth injection. After injecting 15 mL of solution, the product in the basket evolved into more of a thin film rather than spheres.

Experiments 8 and 9 explored minor variations in the broth composition by increasing the concentration of HMTA and urea. The product in experiment 8 initially appeared to be large spheres and after pulling the catch basket from the oil the spheres on top looked to have aged more and to be in a more stable form than those on the bottom. After washing, many of the spheres seemed to break down but many gelled spheres were still observable. During experiment 9 the oil backed up into the injection system at first so the pressure was increased to nearly 6 psi. This released in too much broth being released at once and created a sludge-like surface on the bottom of the catch basket.

Experiments 10 to 12 were the first tests performed using the gelation column described in Section 3.1.2, although the forced air system and broth chamber were still used. It was evident during experiments 10 and 11 that the air flow system was forcing the broth out of the injection system too fast and agitating the oil. Problems also persisted with the broth freezing or gelling early in the line leading up to the point of injection. Experiment 12 was the final run carried out using the forced air system and broth chamber. A pressure of less than 0.5 psi was used but the broth was still being injected too fast for spheres to be formed with a consistent, reproducible geometry. At this point, the system development was put on hold while a series of small scale process development tests were performed to determine the broth composition that would produce fastest gelling spheres (the results from these tests are described in Section 4.2.1).

4.1.3 Syringe Insertion: Manual Injection (Exp. 13 to 16)

Following completion of the small scale tests (Section 4.2.1), the forced air system was removed and a syringe was used to manually inject the broth into the tubing rather than the forced air system. Experiments 13 to 16 were all performed with a 2.13 M solution of HMTA and urea and a 1 M solution of cerium nitrate, as this was the fastest gelling concentration found through the small scale tests. The oil flowing through the system was 100^{o}C, as measured before flowing into the gelation column. However, the needle size was varied to explore differences in sphere formation. Experiments 13, 14, 15, and 16 used 18, 30, 24, and 24 gauge needles respectively (corresponding to 0.838, 0.140, and 0.292 mm inner diameters). In experiment 16 the needle was placed in

the freezer in an effort to prevent clogging by not allowing the broth material to increase in temperature until it is injected into the stream of oil. Experiments 13, 15, and 16 all produced spheres that were able to be aged and washed with hexane and a 0.1 M solution of ammonium hydroxide. All were placed into an 80^{o}C oven overnight to expedite the drying process. Upon examination the next day, those from 15 and 16 appear to have crumbled during the drying process, while 13 remained in good shape (Figure 9). No spheres were produced from experiment 14 as the needle became clogged and only a coating of unformed gel material was obtained.

The spheres produced during experiments 13 through 16 were of varying sizes due to the uneven manual injection rates. When injected too fast, either large spheres or unformed gel was produced.

4.1.4 Syringe Insertion: Automated Injection (Exp. 17 and 18)

The automatic syringe pump was added for experiment 17 and 18. The syringe pump was added to inject the broth into the oil at a constant rate and avoid the problems of inconsistent sphere size that occurred in Section 4.1.3. By using the pump, a steady slow injection rate could be obtained. This also allowed the attention of the operator to be focused elsewhere.

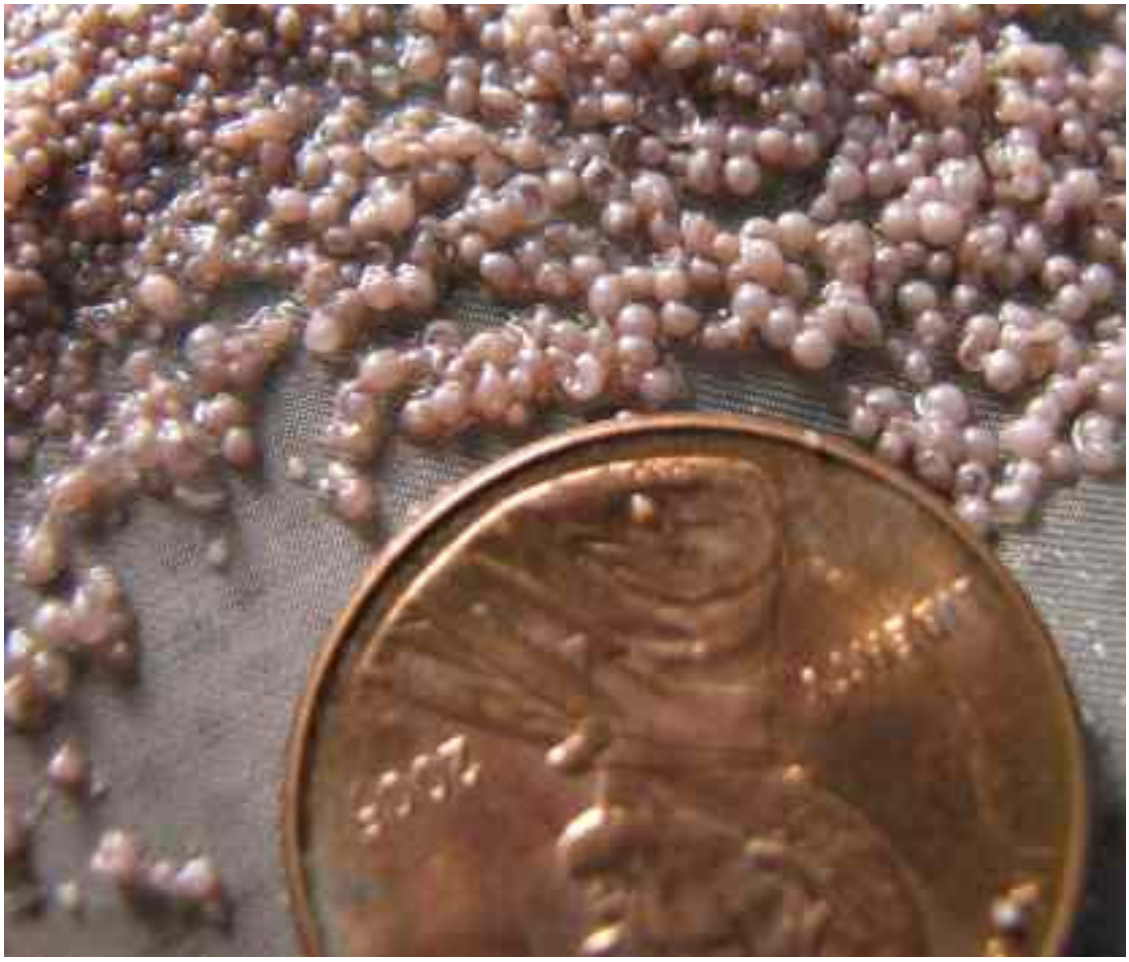

Figure 9. Photograph of product obtained from experiment 13.

The same broth composition and washing procedures from experiments 13 to 16 were used (2.13 M HMTA and urea and 1 M cerium nitrate), as various chilled needles and injection rates were used on the syringe pump. During the course of the run the pump would be stopped and a new needle added for testing. A 26 gauge needle (0.241 mm) and an injection rate of 0.2 mL/min was finally decided upon and used for a majority of the run. Also tested were needles of 22 and 24 gauge (0.394 and 0.292 mm) and injection rates between 0.15 and 0.33 mL/min. The spheres produced were washed

in hexane then in 0.1 M ammonium hydroxide. Experiment 18 used the same broth, temperature, and washing parameters as 17, although with a varied injection rate and only a 26 gauge needle.

Both experiments produced a large number of spheres that were free flowing when removed from the oil rather than fixed in place. When examined the next day after being placed in a 40^{o}C oven, the spheres from both appeared to have either popped or crumbled.

At this point, the system evolution was complete and the remaining experiments were focused on the process chemistry. The system remained relatively unchanged for the rest of the experiments.

4.2 Process Development Experiments

This section describes the series of small scale tests completed between experiments 12 and 13 as well as the process development experiments numbered 19 through 66. The focus of this section is on the development of optimum processing conditions to produce solid cerium oxide microspheres. The process variables that were studied include the broth concentration, oil temperature, aging time, and washing conditions.

4.2.1 Small Scale Internal Gelation Experiments

Between system development experiments 12 and 13, a series of 38 small-scale process development experiments were performed in test tubes using small quantities of HMTA, urea, and cerium nitrate to quantify the gelation time as a function of broth composition. All test solutions were taken from the stock solutions prepared with concentration of 3.2 M HMTA and urea and 3.0 M cerium nitrate. The test tube solutions were prepared containing 1 mL of 3.0 M cerium nitrate and between 1 and 2.1 mL of 3.2 M HMTA and urea. This corresponds to a volume ratio of HMTA and urea to cerium nitrate of 1 to 1 and 2.1 to 1.

Once the solutions were mixed, the test tubes were immediately placed in a beaker filled with silicone oil heated to 100^{o}C and the solution was stirred until gelation occurred. The time to gelation for these experiments was defined to be when the solution fully underwent its color change to white. All data from the series of tests is listed in Appendix B. A trend was seen showing that the tests completed with higher volumes of HMTA and urea tended to have a shorter gel time per milliliter of solution present (Figure 10). The ratios shown in the plot correspond to volume of HMTA and urea within the test (both the same), and dividing it by the volume of cerium nitrate.

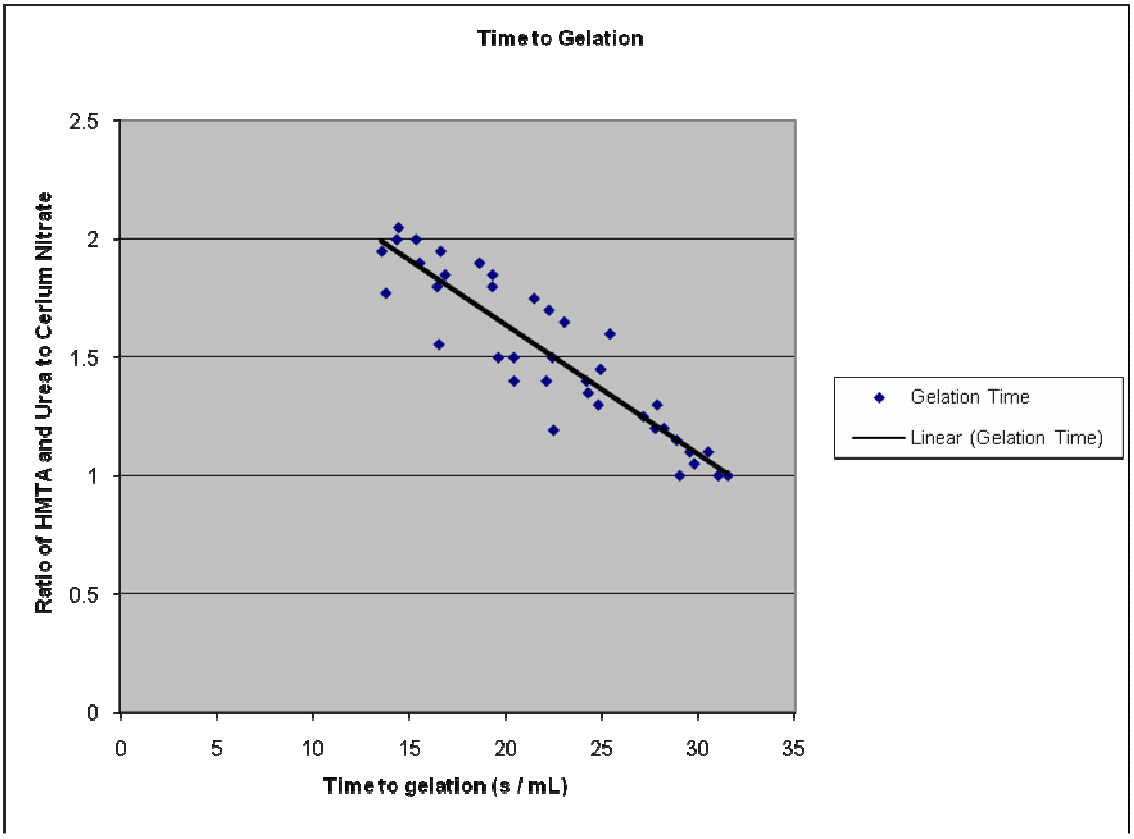

Figure 10. Plot of broth concentration versus time to gelation.

From the data in Appendix B and Figure 10, an HMTA+urea to cerium nitrate volume ratio of 2 to 1 was selected because of the rapid gelation time. This ratio corresponds to a broth concentration with 2.13 M HMTA, 2.13 M urea and 1 M cerium nitrate. This concentration was used to prepare a small solution that was loaded into a syringe and manually injected into the gelation column; the result was that if injected slowly enough, spheres were formed. Approximately 5.5 mL of solution was injected and, after being allowed to age, many noticeable spheres were formed with a small amount of unformed gel material connecting them. This was the first manual syringe

test and it was followed by the system development tests described in Section 4.1.3. From these small scale tests and the introduction of the syringe insertion method, it was possible for the system development stage (Section 4.1) to near its end and begin the process development.

4.2.2 Chemical Feed Variations (Exp. 19 to 36)

Experiments 19 to 36 were carried out to evaluate the impact of varying the broth concentrations to determine the composition of broth that would produce solid spheres when fully washed and dried. In addition, the temperature of the broth was altered, various needle sizes were used, and aging times were varied. It was observed that needle contamination was an important issue; needles not entirely cleaned clogged prematurely. The test conditions for this series of experiments are laid out in Table 1. From these tests, it became evident that increased levels of HMTA and urea produce spheres that are already cracked when removed from the oil. (The practice of placing the broth into the freezer before the experimental run rather than just using an ice bath was also started in the experiments described in this section.)

Table 1. Conditions for experiments 19 through 36.

Exp.	HMTA/Urea Conc.	Cerium Nitrate Conc.	Oil Temperature (^{o}C)	Needle Size (ga)	Aging Time (min)
19	1.92 M	1.2 M	100	26	20
20	1.78 M	1.33 M	100	26 (f)	15
21	1.68 M	1.43 M	100	24	15
22	1.78 M	1.33 M	100	24 (f)	30
23	1.78 M	1.33 M	100	18	30
24	1.68 M	1.3 M	100	24 (f)	45
25	1.6 M	1.5 M	100	26 (f)	---
26	1.92 M	1.2 M	110	24 (f)	30
27	1.78 M	1.33 M	110	24 (f)	---
28	1.6 M	1.5 M	100	22 (f)	30
29	1.64 M	1.46 M	100	22 (f)	120
30	1.68 M	1.3 M	100	22 (f)	30
31	1.62 M	1.48 M	100	22 (f)	30
32	1.68 M	1.3 M	100	22 (f)	---
33	1.64 M	1.46 M	100	22 (f)	---
34	1.52 M	1.58 M	100	18 (f)	30
35	2.06 M	1.07 M	100	18 (f)	30
36	1.42 M	1.67 M	100	18 (f)	30

(f) connotes that the needle was placed into a freezer prior to the experimental run.

With the exception of experiment 35, performed with a 2.06 M solution of HMTA and urea, all were carried out with 1.92 M solutions or less and all were performed at 100^{o}C except for experiment 27 performed at 110^{o}C. Experiments 19, 20, and 21 involved decreasing concentrations of HMTA and urea and increasing levels of cerium nitrate. The results of all three were then allowed to age for 15 to 20 minutes, washed in hexane, and then in a solution of 0.1 M ammonium hydroxide. The product from experiment 19, after removal from a low temperature oven, appeared cracked with some of the remaining spheres not hollow. While washing the spheres from experiments 20 and 21, the ammonium hydroxide wash appears to break down the spheres and leave a sludge surface on them. After one day, the spheres from experiment 20 were solid while those from experiment 21 were hollow and cracked.

Experiments 22 and 23 were both completed with a cerium nitrate concentration of 1.33 M and a 1.78 M solution of HMTA and urea. Both produced solid spheres after injecting over 3 mL of solution and washing in hexane. When washed in 0.1 M ammonium hydroxide, the product of experiment 22 became cloudy and formed a crud layer. Washing of experiment 23 was terminated after the hexane wash. When examined after drying, the spheres did not appear cracked or hollow (Figure 11). Experiment 24 decreased the HMTA and urea ratio slightly and produced spheres that were free flowing when washed in hexane. The product was then rinsed in water rather than an ammonium hydroxide wash, although the same results were obtained.

Figure 11. Picture of product obtained from experiment 23

Experiments 26 through 31 began another series of decreasing HMTA and urea concentrations while also raising the amount of cerium nitrate. The oil temperature was raised to 110^{o}C in experiment 26 and the product was washed with hexane and water. After drying, the spheres were observed to be hollow, as had been observed in previous experiments. Experiment 28 lowered the temperature back to 100^{o}C and stopped the wash process after hexane. The product obtained had an excess of white unformed gel

that appeared to be formed around many of the spheres. After drying, many of the formed spheres did not appear to be hollow when observed under an optical stereo microscope. Experiment 29 used a further decrease in the HMTA and urea concentrations and a longer aging time of two hours before removal from the oil. The product appeared to be made of spheres of two different colors. The first group was white with a slight pink tint that appeared solid. The second product was a lavender color that cracked and crumbled during the hexane wash, as seen in Figure 12.

Figure 12. Photograph of dried product from experiment 29.

For experiment 30 the HMTA and urea concentration was increased and the resulting product contained more of the white spheres with the crumbly lavender spheres in the minority. Experiment 31 lowered the HMTA and urea ratio to below the level for experiment 29 and obtained a product that consisted of spheres connected by unformed gel. When washed in ammonium hydroxide, the unformed material was partially removed leaving only the spheres connected by unformed gel, shown in Figure 13.

Figure 13. Photograph of product obtained from experiment 31.

Experiment 33 began the practice of placing the unmixed broth into a freezer approximately an hour before being injected into the system. The concentration was the same as experiment 31 and roughly the same product was obtained. Experiment 34 was carried out with a cerium nitrate concentration of 1.58 M and a 1.52 M concentration of HMTA and urea. After 30 minutes of aging, the product contained many spheres connected by unformed gel that remained after the hexane wash. Experiment 35 was performed with a concentration of 2.06 M HMTA and urea and 1.07 M cerium nitrate; this combination was produced by operator error. The product contained unformed gel, white spheres, lavender spheres, and dark spheres already cracked. Experiment 36 was performed with a cerium nitrate concentration of 1.67 M and HMTA and urea of 1.42 M. This experiment was also the first to use baskets made of 80 x 80 wires per inch stainless steel mesh and of a smaller overall size. Results obtained for this run were some spheres with an excess of unformed gel connecting them. After washing in hexane it was discovered that even the new baskets would not allow the ammonium hydroxide to drain during the washing process.

Experiments 25, 27, and 32 were all terminated early as the syringe began gelling before a significant portion of broth could be injected into the system.

4.2.3 Narrowed Broth Concentration (Exp. 37 to 48)

Experiments 37 to 48 were all carried out with cerium nitrate concentrations between 1.44 and 1.46 M with HMTA and urea molarity spanning 1.65 to 1.67 M. From previous results in Section 4.3.1, it was found that the spheres that stood up the best after being dried came from this range and therefore these conditions were warranted. All

tests were performed at 100^{o}C, an 18 gauge needle, and 30 minutes of aging time, as seen in Table 2. Wash conditions for this portion of the experiments were varied. The initial experiments were washed in hexane and 0.1 M ammonium hydroxide. A portion received only a hexane wash after it was discovered the dried product was not cracked and crumbling using this method. The final series underwent hexane a hexane wash and then an ammonium hydroxide varied from 0.5 to 3 M.

Experiments 37 and 38 were carried out with slight variations of concentrations of solution and identical operating conditions after finding the optimum injection rate for an 18 gauge needle, 0.1 to 0.2 mL/min. Initial examination of experiment 37 showed a wide variety of spheres due to the varying injection rates. After washing in hexane and then a solution of 0.1 M ammonium hydroxide, the product appeared to remain solid. The spheres were then rinsed with water and placed in a 60^{o}C oven overnight to dry. The final dried product was partially cracked, with a portion of the spheres sticking to each other during the drying process. Experiment 38 started at the lower end of the injection rate span identified in experiment 37 then moved to the middle of that span. When first removed from the oil after aging 30 minutes the spheres are all white in color with a minimum amount of unformed product. After the hexane wash a solution of 0.1M ammonium hydroxide was used that appeared to dissolve a majority of the spheres.

Table 2. Conditions for experiments 37 through 48.

Exp.	HMTA/Urea Conc.	Cerium Nitrate Conc.	Oil Temp. (^{o}C)	Needle Size (ga)	Aging Time (min)
37	1.66 M	1.44 M	100	18 (f)	30
38	1.65 M	1.46 M	100	18 (f)	30
39	1.65 M	1.45 M	100	18 (f)	30
40	1.65 M	1.46 M	100	18 (f)	30
41	1.67 M	1.44 M	100	18 (f)	30
42	1.65 M	1.45 M	100	18 (f)	30
43	1.65 M	1.45 M	100	18	30
44	1.65 M	1.45 M	100	18	30
45	1.65 M	1.46 M	100	18 (f)	30
46	1.65 M	1.45 M	100	18	30
47	1.65 M	1.45 M	100	18	30
48	1.65 M	1.45 M	100	18	30

Since it appeared that the ammonium hydroxide wash was breaking down the spheres, the product from experiments 39 through 41 was only washed in hexane. The product obtained from experiment 39 was placed into a warm oven overnight to dry, and when examined the next day had not broken down in any way, shown in Figure 14.

Experiment 40 involved a slightly lower HMTA and urea concentration and a needle change was required almost immediately as the first became clogged. The final

washed and dried product did not turn out as well as experiment 39. Connecting the spheres was unformed gel that remained after the hexane wash. Experiment 41, using the highest of the HMTA and urea concentrations, obtained a product that was similar to 39. The products from all three of these runs retained a wet, slightly oily look to them, even after being allowed to dry in the oven. This was caused by too short of a hexane wash or the lack of an ammonium hydroxide wash. Experiment 42 used the same broth concentrations as 38, although the needle clogged quickly and was replaced. After 0.857 mL of broth was injected, the entire syringe began to gel and injection was stopped at this point. During the hexane wash it was discovered there was a hole in the bottom of the basket that allowed all the spheres to escape into the beaker. After the wash was finished, a second wash was then performed using a 3 M solution of ammonium hydroxide. The spheres did not break down during this wash, and after the wash completed the spheres were placed onto a mesh screen to dry.

Figure 14. Photograph of product from experiment 39.

Beginning with experiment 43, the needles were no longer placed in the freezer after the previous few experiments utilizing this method experienced clogs early in the runs. Experiments 43 and 44 both used a cerium nitrate solution of 1.45 M and a 1.65 M solution of HMTA and urea. After aging 30 minutes, the spheres were found to be of a high quality, appearing like those of 39 (Figure 14). The product from 43 was only washed in hexane, while half of those from 44 were washed in two 40 minutes washes of

3 M ammonium hydroxide. The next day those washed in hexane only remained intact, while the portion washed in ammonium hydroxide appear chalky and were crumbling. Experiment 45 used a broth solution that had been prepared the previous day and kept in the freezer overnight. When injected into the oil solution, the spheres began to gel well down in the column, rather than halfway up as had been observed in previous experimental runs. After 2.5 mL of injection, two needles had become clogged and were replaced by interrupting the experiment. The product was allowed to age for ~30 minutes. After washing in hexane and dried, the product was very sticky with few well defined areas of spheres. The needle clogging and needing replacement contaminated the system and caused the poor quality of the product.

Experiments 46 through 48 comprised an investigation to determine the proper molarity of ammonium hydroxide in the post hexane wash. All three experiments used the same broth concentration as experiment 39, which had the best product spheres from the previous runs (1.65 M HMTA and urea and 1.45 M cerium nitrate). Experiment 46 experienced no clogging and the spheres aged for 30 minutes. Once the hexane wash was completed, half of the product was washed in two consecutive steps of 3 M ammonium hydroxide then rinsed in water. After drying, this product was cracked and crumbling. The products from experiments 47 and 48 were also washed with hexane and then split into two groups for individual washes of varying ammonium hydroxide molarity followed by a rinse in water. The two washes for experiment 47 were 2 M and 1 M for 40 minutes, and experiment 48 used solutions of 0.75 M and 0.5 M for slightly

under 40 minutes. One day later, both of the washed products from 47 appeared dry and cracked, and those from 48 appear a mess of material, shown in Figures 15 and 16.

Figure 15. Product from experiment 47 washed in 2 M ammonium hydroxide.

Figure 16. Product from experiment 48 washed in 0.5 M ammonium hydroxide.

4.2.4 Multi-Stage Washing (Exp. 49 to 53)

The next sequence of experiments was performed to further refine the wash procedure. Even though spheres washed in hexane and not ammonium hydroxide were the only ones to remain solid after washing, the lack of a complete wash resulted in unreacted product on the outside and within the spheres. If this is not removed, sintering of the spheres cannot occur. All experiments from this point used catch baskets with the bottom portion produced from 40 x 40 wires per inch stainless steel mesh. This bottom allows complete washing of the spheres within the baskets without the need to remove

the product from the basket. This change allowed the ammonium hydroxide wash solution to completely drain during the wash.

After the failed attempts above of washing the microspheres in ammonium hydroxide using a 1.45 M solution of cerium nitrate and a 1.65 M solution of HMTA and urea (Section 4.2.3), changes were made in the concentrations of experiments 49 through 53 in an attempt to find a solution that would withstand washing. These changes are outlined in Table 3, which shows how the concentrations of HMTA and urea were increased within the broth solution. In this series, the spheres were washed with hexane and then washed using several wash stages with varying concentration of ammonium hydroxide.

Table 3. Conditions for experiments 49 through 53.

Exp.	HMTA/Urea Conc.	Cerium Nitrate Conc.	Oil Temp (^{o}C)	Needle Size (ga)	Aging Time (min)
49	1.68 M	1.43 M	100	18	30
50	1.75 M	1.36 M	100	18	30
51	1.81 M	1.3 M	100	18	30
52	1.68 M	1.3 M	100	18	30
53	1.68 M	1.43 M	100	18	30

Experiment 49 used a cerium nitrate solution of 1.43 M and a 1.68 M solution of HMTA and urea. After the hexane wash, two consecutive washes of 3 M ammonium

hydroxide were performed for 40 minutes each followed by a water rinse. After drying, the spheres crumbled, though some remained intact with an off white color and solid, shown in Figure 17.

Figure 17. Photograph of dried product from experiment 49.

Starting with experiment 50, the 3-stage wash system used at Oak Ridge National Laboratory for UO_2 was implemented [13]. The wash, a three step process for 60 to 75 minutes each, consists of a first wash in a solution of 50% isopropyl alcohol and 50%

1.5 M ammonium hydroxide. The next step is a 0.5 M solution of ammonium hydroxide. The final stage involves a solution of 75% isopropyl alcohol and 25% water [13].

Experiments 50 through 53 were all carried out with slightly raised amounts of HMTA and urea and a lower concentration of cerium nitrate. After aging 30 minutes and undergoing a hexane wash, in the product form experiment 50 did not appear to stick together as they had in previous washes. When dried, the spheres appear cracked and crumbling. The spheres produced in experiment 51 were darker in color than those of 50, and they began breaking down during the first step of the wash. The spheres produced in 52 and 53, after aging for 30 minutes, appeared solid with no visible cracking after the wash process. They were then placed into a warm oven overnight to dry. As with the previous experiments, the dried product was cracked and crumbled into powder, Figure 18 shows the product from experiment 53.

Figure 18. Photograph of dried product from experiment 53.

4.2.5 Constant Broth Concentration (Exp. 54 to 59)

Experiments 54 through 59 were all run with the same broth concentrations used in experiment 39 (Section 4.2.3), 1.45 M for cerium nitrate and 1.65 M for HMTA and urea, which had produced the best dried spheres to this point. These experiments evaluated variations of temperature of the oil, amount of time for aging, and the initial wash steps. Table 4 details the conditions for each of the experiments.

Table 4. Conditions for experiments 54 through 59.

Exp.	HMTA/Urea Conc.	Cerium Nitrate Conc.	Oil Temp (^{o}C)	Needle Size (ga)	Aging Time (min)
54	1.65	1.45	100	18	30
55	1.65	1.45	100	18	60
56	1.65	1.45	100	18	90
57	1.65	1.45	100	18	60
58	1.65	1.45	100	18	0
59	1.65	1.45	90	18	60

Experiments 54 and 55 were completed with an aging of 30 and 60 minutes respectively then washed in hexane. After the full wash process, 54 was placed into a 40^{o}C oven overnight to dry, while 55 was placed in front of a fan for forced convection at room temperature. Examining each of them the next day revealed that the product from experiment 54 was dry and cracked and the product from experiment 55 also appeared dry and crumbling at first. However, under a microscope many of the spheres from experiment 55 were found to be solid with no hollow sections. Experiment 56 was aged for 90 minutes and washed in hexane. After removing from the oil, the spheres did not look to be the same quality as previous experiments. During the second stage of the wash process, 50% solution of 1.5 M ammonium hydroxide and 50% isopropyl alcohol, the basket failed and the spheres were released into the beaker. After the wash step was finished, the spheres were placed onto a screen and placed in front of a fan to dry.

Examining the next day showed the spheres to very brittle with cracking also occurring, shown in Figure 19.

Figure 19. Photograph of dried product from experiment 56.

Experiment 57 was aged for 60 minutes then the hexane wash was skipped in an effort to produce better washed spheres. After the rest of the washing process, the spheres were placed in front of a fan for 15 minutes to dry. The final dried product was cracked and crumbling. The change made for experiment 58 was to allow no aging to

occur after 3.65 mL of solution was injected. The product was immediately washed in hexane for 10 minutes and then underwent the rest of the wash process before being placed in front of a fan to air dry. The next day, it was observed that the product had some dark spheres and some lighter colored ones that appeared to remain solid. Experiment 59 was run at a temperature of 90^{o}C and allowed to age for 60 minutes before being washed in a hexane solution. When removed from the oil there was an abundance of unformed gel present in the basket. Gelation had not occurred until near the bottom of the gelation column, whereas normally it occurred near the halfway point. When gelation does not occur in the column, the droplets do not have an opportunity to gel into a spherical shape before being deposited into the catch basket. During the first stage of the wash process the basket failed, as had happened in experiment 56. After finishing the 60 minute wash, the product was rinsed in water before being allowed to dry in front of a fan. It was noticed when undergoing the first wash stage that most of the unformed gel dissolved when lowered into the wash. The product appeared cracked and crumbling when examined the next day.

4.2.6 Feed Broth Dilution (Exp. 60 to 66)

Experiments 60 through 66 involved the addition of water to the broth solution of HMTA, urea, and cerium nitrate in an attempt to obtain spheres that would better withstand the washing process. This series of experiments was performed with dilution to examine the possibility that the overall broth solution was too strong and dissolving itself during the drying process. For experiments 60, 61, 62, and 66, the same initial concentrations (1.45 M cerium nitrate and 1.65 M HMTA and urea) were used as in

Section 4.2.5, but with varying amounts of water added to dilute the solution. Conditions for experiments 60 through 66 are shown in Table 5.

Table 5. Conditions for experiments 60 through 66.

Exp.	HMTA/Urea Conc.	Cerium Nitrate Conc.	Oil Temp (^{o}C)	Needle Size (ga)	Aging Time (min)
60	1.48	1.29	100	18	30
61	1.42	1.25	100	18	60
62	1.56	1.37	100	18	30
63	1.35	1.05	100	18	30
64	1.65	1.29	100	18	30
65	1.64	1.46	100	18	60
66	1.62	1.42	100	18	30

Experiment 60 used a 1.29 M solution of cerium nitrate and a 1.48 M solution of HMTA and urea and the product was aged for 30 minutes and washed in hexane for 10 minutes. After finishing the 3-stage wash process described above, the spheres were placed in front of a fan to air dry. The dried product appeared mostly dark and cracked, although a portion of the product was better than in previous experiments. Experiment 61 used a broth consisting of a 1.25 M solution of cerium nitrate and a 1.42 solution of HMTA and urea. After injection, the product was aged for 60 minutes and had a large amount of unformed gel when removed from the oil. The product was washed in hexane

and then underwent the full wash where most of the unformed gel was removed during the first step. The finished product was semi-spherical and caked together. Experiment 62 used a 1.37 M solution of cerium nitrate and a 1.56 M solution of HMTA and urea. This product was allowed to age for 30 minutes and then underwent a 25 minute hexane wash before continuing with the rest of the wash process. The final product was a yellowish powder with a few solid spheres scattered throughout, as seen in Figure 20.

Figure 20. Photograph of dried product from experiment 62.

Experiments 63 and 64 were completed with the same initial broth concentrations (1.36 M cerium nitrate and 1.75 M HMTA and urea) before water was added to dilute the solutions. Experiment 63 was run with a solution of 1.05 M cerium nitrate and 1.35 M HMTA and urea. This was originally not meant to be as diluted, however an error occurred during addition of the water. Gelation occurred near the bottom of the column, if at all, for this broth solution. After aging for 30 minutes it was noted that a few spheres were present in the catch basket as well as a large volume of unformed gel. In the hexane wash a portion of the unformed gel broke down, and after the first step of the wash process, it was canceled since all that remained was sludge. The final dried material was just a layer of gel with a few spheres present within. Experiment 64 used a much less diluted solution of 1.29 M cerium nitrate and 1.65 M HMTA and urea. After aging for 30 minutes the product was then washed in hexane. During the first step of the wash process the bottom fell off the basket once again. All steps of the wash process were completed, although for 75 minutes rather than the typical 60. After being dried, the product appeared even more crumbled than usual.

Experiment 65 decreased the amount of HMTA and urea within the solution to below the level used in Section 4.2.5, as this had not been attempted since beginning the full wash system. After aging for 60 minutes it was noticed that in addition to the spheres, there was unformed gel present in the basket. The spheres that were present were oblong and not spherical in shape. The product was washed in hexane and the 3-stage ammonium hydroxide process, where most of the unformed gel dissolved during the first stage. Not many spheres remained after the stage washing, and after being dried

they appeared cracked, but not as crumbling as those from 64. Experiment 66 was the final one performed with a diluted broth solution. When the product was pulled from the oil there was quite a bit of unformed gel present mixed in with the spheres. During the wash process the unformed gel dissolved leaving only the spheres. The dried spheres appeared crumbling and cracked.

4.3 Microsphere Production and Characterization

Over the span of the previous 66 experiments it was observed that the highest quality microspheres were produced from a broth of 1.45 M cerium nitrate and 1.65 M HMTA and urea. Also observed was that if the temperature of the oil is too low, the spheres will not form until near the bottom of the column, generally resulting in the production of unformed gel. The final set of experiments used the ideal broth composition and the final two experiments raised the temperature of the oil above the 100^{o}C that had been common.

Following the completion of the experimental series, a number of analysis techniques were performed on the microspheres. To sinter the spheres and identify the presence of any reaction occurring during the process, Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) were performed to evaluate the mass changes and identify any possible reaction during the heating process. Also, x-ray diffraction (XRD) was used to characterize the crystal structure and identify the phases present in the product microspheres.

4.3.1 Increased Oil Temperature (Exp. 67 to 70)

It was observed previously that the highest quality spheres came from a broth composed of 1.45 M cerium nitrate and 1.65 M HMTA and urea. The final experiments completed, 67 through 70, all used this broth composition. Varied for the experimental series was the temperature of the oil and the aging and wash times, as shown in Table 6.

Table 6. Conditions for experiments 67 through 70.

Exp.	HMTA/Urea Conc.	Cerium Nitrate Conc.	Oil Temp (^{o}C)	Needle Size (ga)	Aging Time (min)
67	1.65	1.45	100	18	30
68	1.65	1.45	100	18	70
69	1.65	1.45	110	18	60
70	1.65	1.45	115	18	60

Experiment 67 did not have any unformed gel when removed from the oil. During the 3-stage washing process it appeared that a large portion of the microspheres were breaking down. The final dried product was cracked and crumbled into powder. Within the dried product, there were a few solid spheres that appeared soft. Experiment 68 suspended the basket above the oil reservoir to ensure equal aging for all spheres. When all the broth was injected, the basket was then lowered into the oil and aged for 70 minutes. After washing and drying, the product was cracked and crumbled into powder.

Experiments 69 and 70 were both performed with higher silicone oil temperatures; 110°C and 115°C respectively. Experiment 26 had been performed with an oil temperature of 110°C, but did not use the broth composition that has been determined to be ideal (1.65 M HMTA and urea and 1.45 M cerium nitrate). Each was allowed to age for 60 minutes, washed in hexane, then underwent washing for 75 minutes in each step of the 3-stage wash process. The final dried product from each was very white and powder like. When examined under a microscope the spheres are solid, but were brittle and crumbled with a small amount of force. Earlier experiments that had produced solid, washed spheres were darker in color, as like those from experiment 56. Product from experiment 69 is seen in Figure 21.

4.3.2 Differential Scanning Calorimetry and Thermogravimetric Analysis

One of the analytical needs for the process development experiments was the characterization of the particles after washing and drying to determine the nature of the solid product from the tests. To this end, Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) measurements were made for a select set of product microspheres using a Netzsch STA 409 PC. Table 7 lists the spheres that were analyzed and the principal results. The goal of the measurements was to determine the thermochemical response to temperature. The DSC measurement involves heating the sample to a set temperature, and then measuring the heat and energy required to heat a reference to the same temperature. As a reaction occurs in the sample, more or less energy is required to keep the reference at the same temperature. The TGA

measurement involves using a fine balance to measure the mass change of the sample as it is heated.

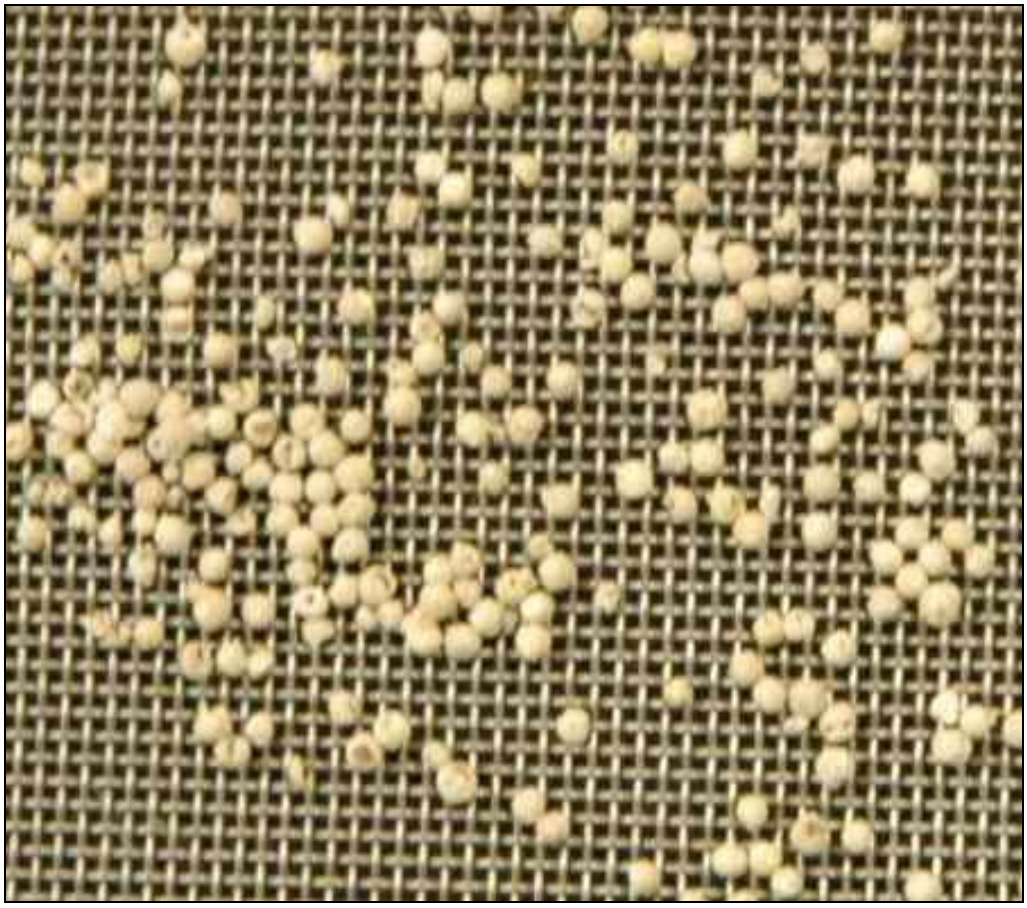

Figure 21. Photograph of product from experiment 69.

Table 7. List of samples analyzed by DSC and TGA methods.

Experiment Number	Type of Analysis	Principal Observations
56	TGA to 1400°C	40% mass loss during exothermic reaction 60% overall mass loss
56	DSC to 1400°C	Exothermic reaction observed at ~205°C
69	TGA to 500°C	Initial mass gain ~40% overall mass loss
69	DSC to 500°C	Exothermic reaction begins ~200°C, but not as sharp as experiment 69
69	TGA to 175°C	Small mass gain observed Gradual loss of less than 6% mass
69	TGA to 300°C	Sharp 6% mass loss at 200°C
69	TGA held 300°C	Slight mass loss as temperature held
70	TGA to 1450°C	Quick mass loss of ~15% at 200°C

For the spheres to be pressed into a cermet storage or fuel form, they must first be able to withstand high temperature and sintered to high density. To examine this requirement, a small portion from experiment 56 underwent a mock sintering profile within the Netzsch STA 409 PC instrument. The spheres were heated under an argon atmosphere and the temperature was increased to slightly over 1400^{o}C at a rate of 10 degrees per minute, held there for 30 minutes, then allowed to cool. This heating profile is shown in Figure 22. The product from experiment 56 was chosen since it was one of the first to be have solid spheres produced from the ideal concentration and to complete at least a portion of the 3-stage wash process.

At roughly 205^{o}C, the DSC data indicated that a strong exothermic reaction occurred and the TGA data revealed that the product mass decreased by nearly 40% at that point (Figure 23). Following this, the mass slowly decreased with temperature. After cooling, the product was removed from the system and the spheres had become a fine gray powder. As mentioned previously, experiment 56 was chosen because the spheres were solid and the result seemed to indicate that the washing step was incomplete.

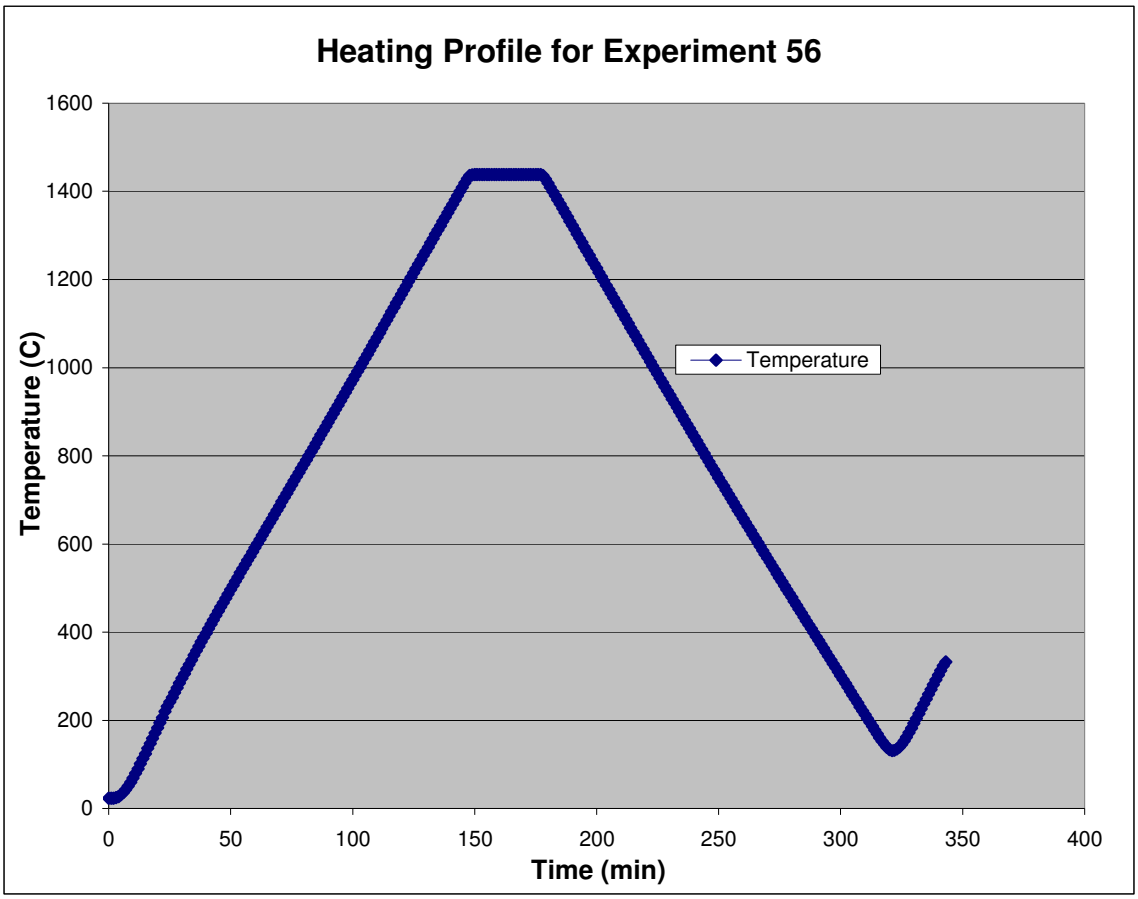

Figure 22. Plot of the heating profile used for experiment 56 sample.

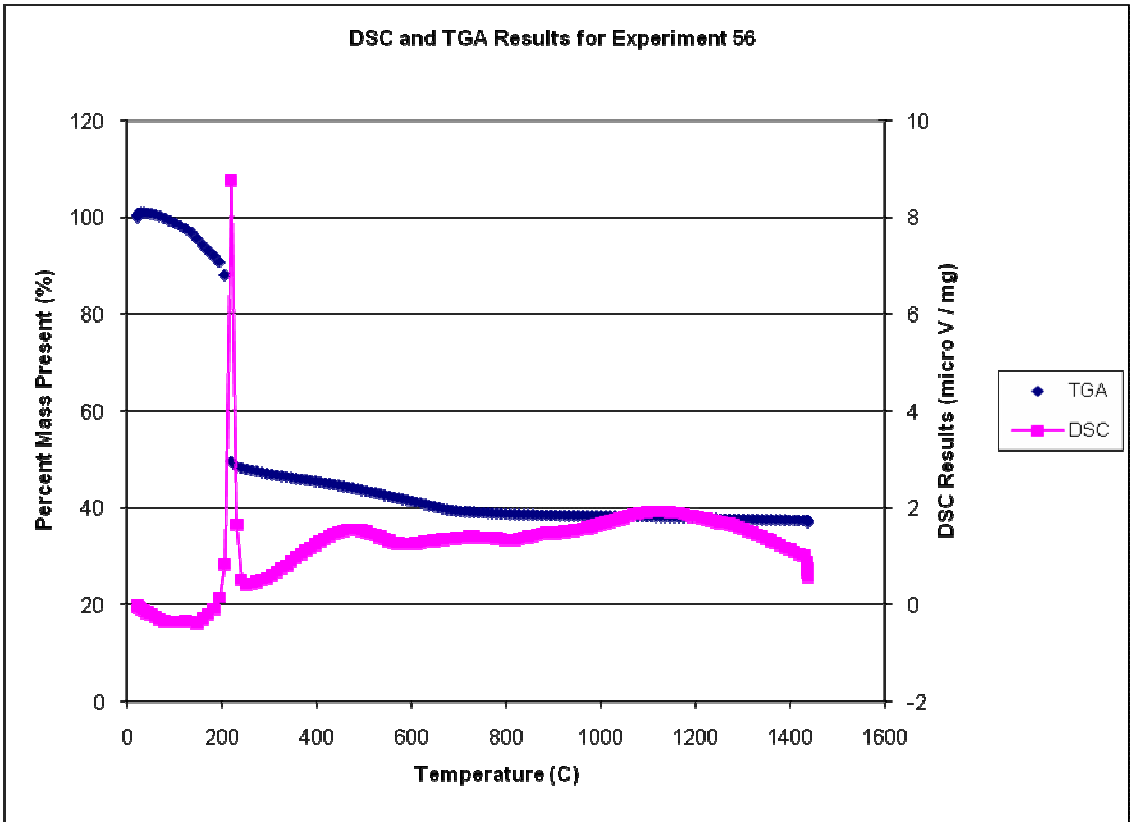

Figure 23. DSC and TGA results for experiment 56.

The second product that was analyzed came from experiment 69. These microspheres were from the final two batches that were well formed, well aged, and well washed. In this test, the DSC/TGA chamber was only heated to 500°C in an argon environment. This temperature was selected because the exothermic reaction occurred at 205°C and the intent of the test was to evaluate the impact of the final optimized processing method on the spheres (see Section 4.3.1 for more detail on the procedures used to generate the spheres. As observed in the previous test, an exothermic reaction was indicated between 200 and 250°C by the DSC trace (Figure 24). In this case the

mass loss was dramatically reduced, indicating that there were fewer leftover reagents in the product spheres.

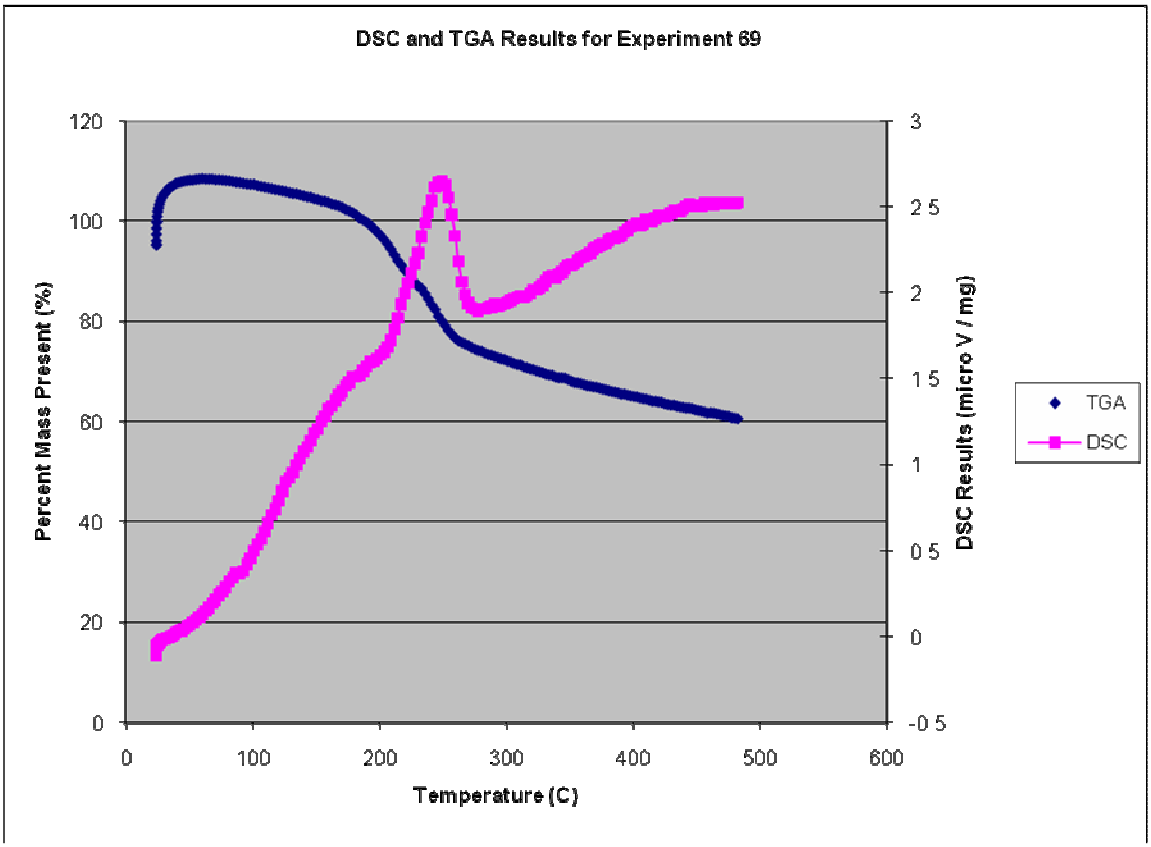

Figure 24. DSC and TGA results for experiment 69.

When removed from the system, the spheres had not swollen and crumbled as they had when product from experiment 56 was tested in the STA. Instead, they had turned from an off white color to a faded yellow, as seen in Figure 25.

Figure 25. Image of spheres from experiment 69 heated to 500°C.

Next, additional product from experiment 69 was used to investigate the nature of the exothermic reaction. The remaining microspheres were split into two batches and separate samples were analyzed using a large TGA sample cup. The first sample was heated to 175°C and held for two hours (Figure 26). The second sample was heated to 300°C (Figure 27). The first of the samples, held below the exothermic reaction temperature of ~200°C, experienced only a small mass loss, ~5%, during the span of its heating (Figure 26). The second sample underwent an exothermic reaction at

approximately 200°C and lost over 12% of its mass in the process (Figure 27). This sample was meant to be heated to 300°C for two hours; however, when this temperature was reached an over temperature safety was thrown and the run was cancelled.

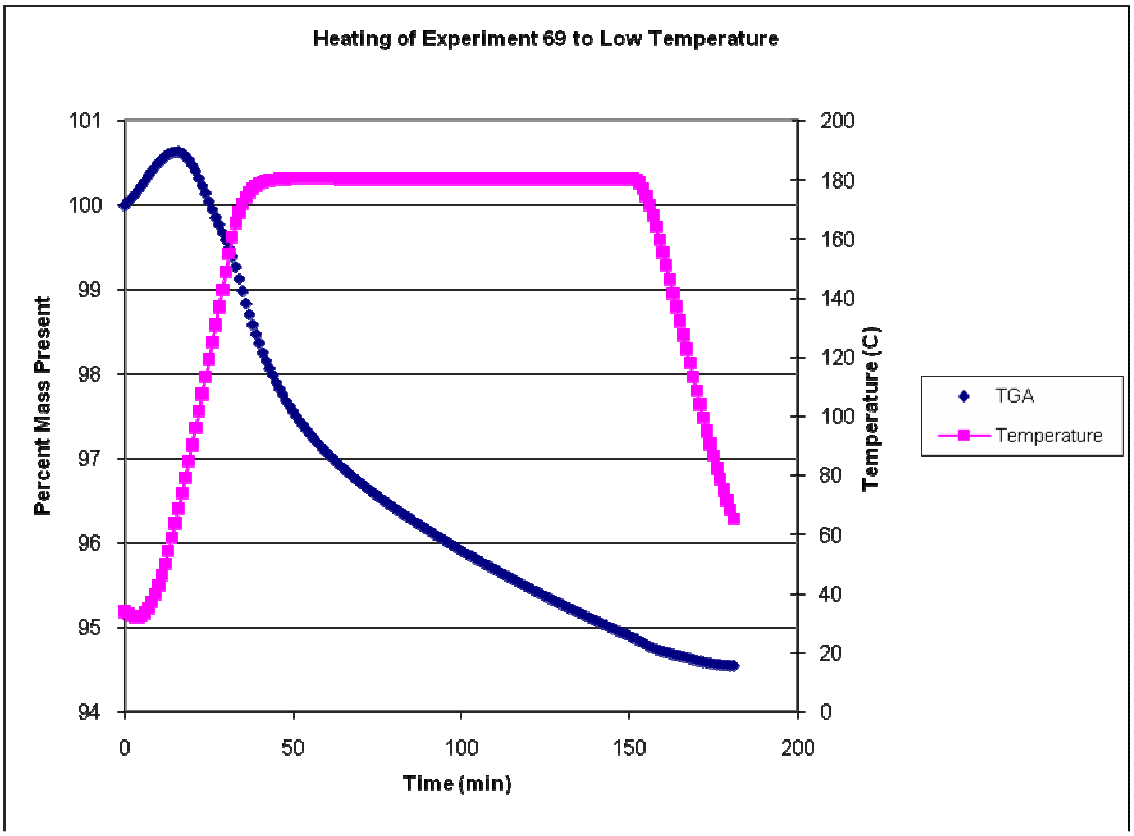

Figure 26. TGA results from heating experiment 69 to below 200°C.

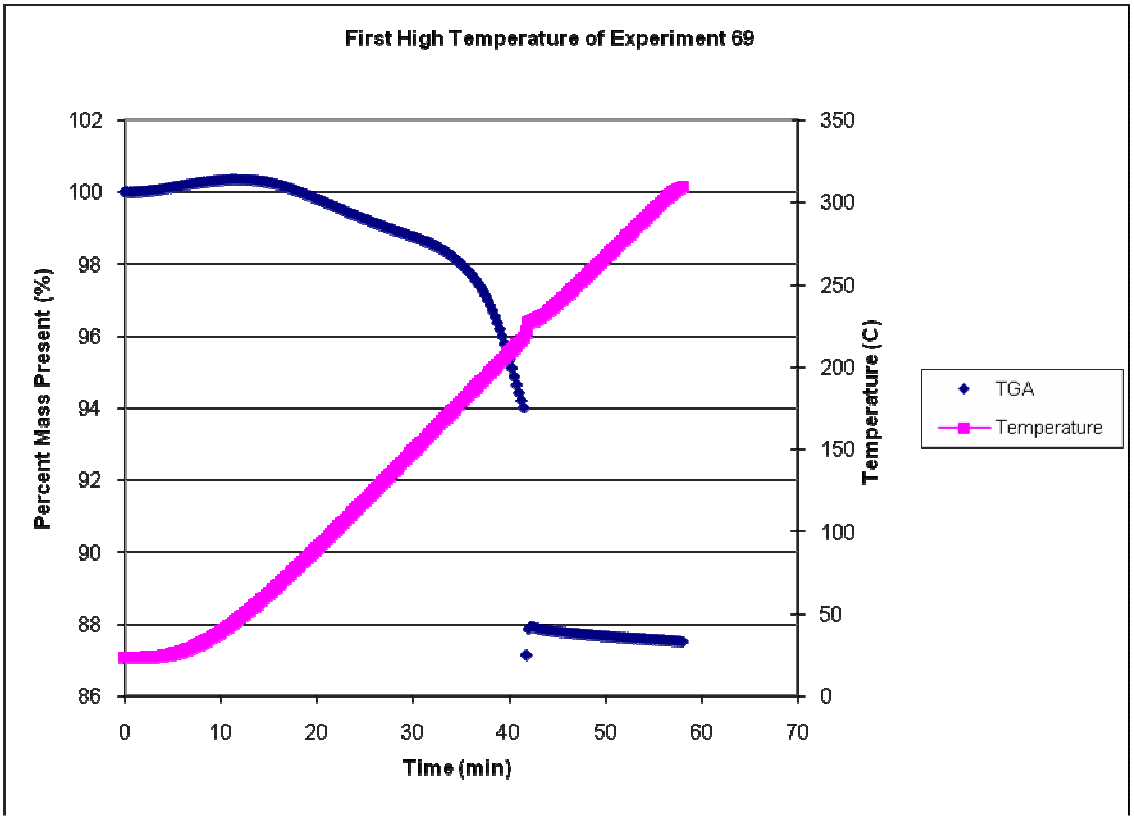

Figure 27. TGA results from heating experiment 69 to 300°C.

When the sample cooled to 210°C the run was reactivated and completed at 300°C for the full two hours (Figure 28). The sample initially gained mass, most likely from being reheated, and the sample proceeded to gradually lose mass as the temperature was held constant, although a much smaller percentage than was observed in the previous runs. When the sample was removed from the system it had turned the same faded yellow color as the small portion that had been heated to 500°C. It is evident from these results that the product from experiment 56 has a significant quantity of volatile reagent left in the spheres whereas the product from experiment 69 had a much lower

amount of this material (but it was still there). The X-ray diffraction data in the following section confirms this observation.

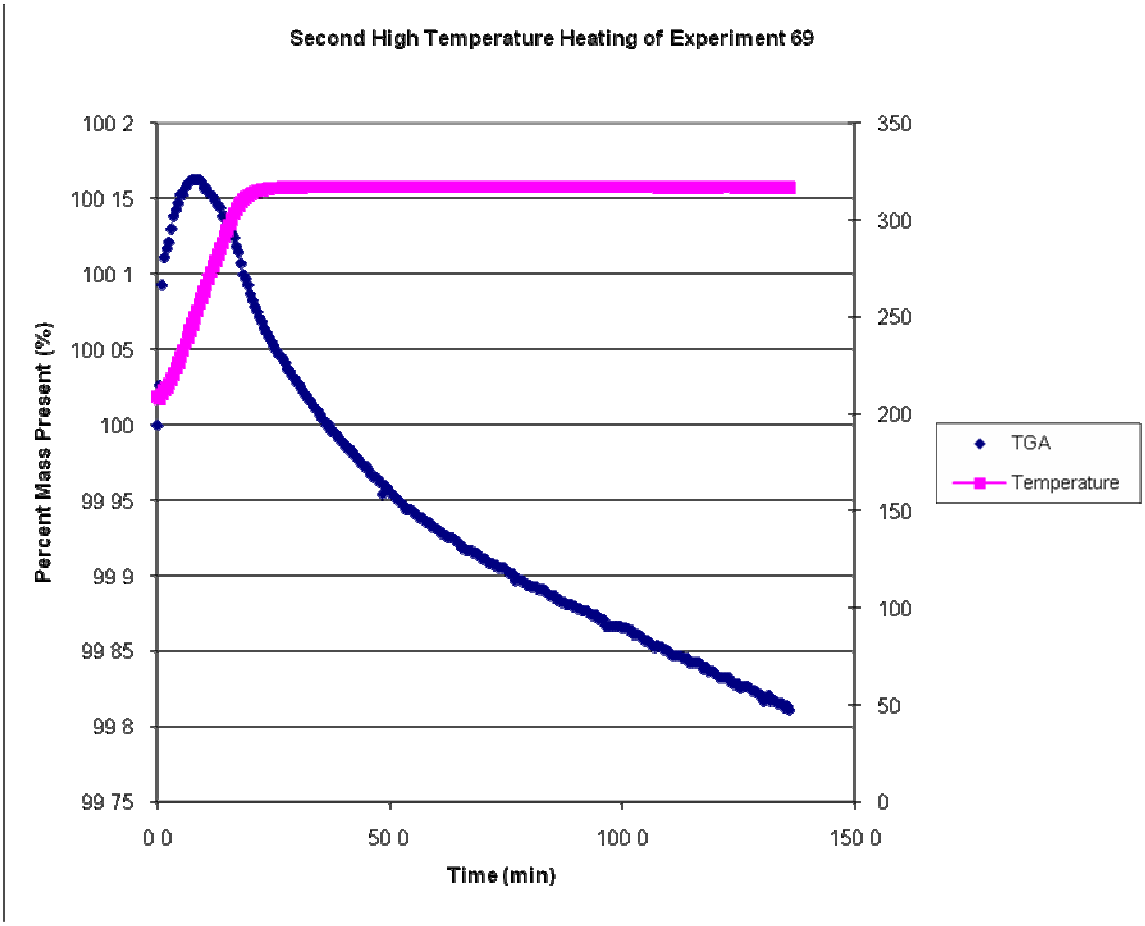

Figure 28. TGA results from holding experiment 69 at 300°C for 2 hours.

None of the spheres from experiment 69 exhibited the same ballooning problem as had affected those from 56, so an attempt was made to take fully washed spheres up to sintering temperatures. However, the entire product from experiment 69 was consumed in the various DSC and TGA trials, so spheres produced from experiment 70

were used instead. The only difference between the two experiments was that experiment 70 was gelled 5°C higher than experiment 69.

The STA instrument was used to sinter a portion of the produce from experiment 70. To do this, the large TGA sample cup was used. The product was heated to 1450°C and held for four hours. Figure 29 shows that the exothermic reaction and mass loss was again evident in this sample at ~200°C. The mass loss was significant, yet not as extreme as seen in experiment 56.

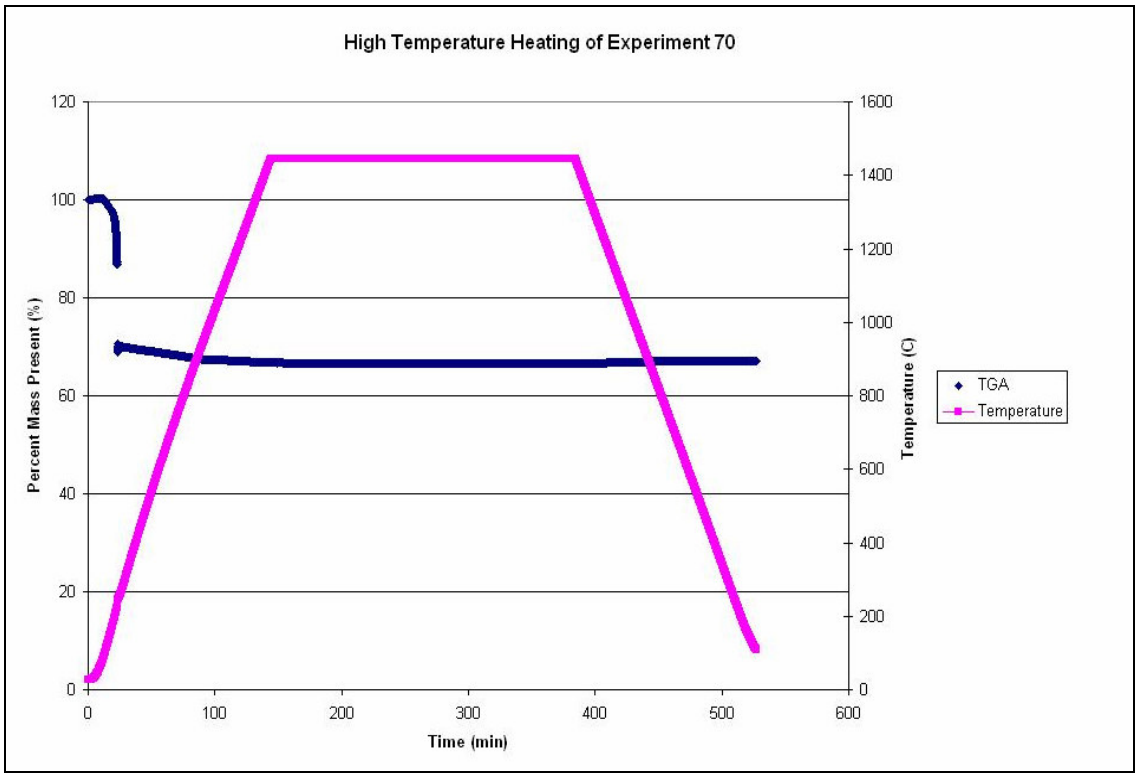

Figure 29. TGA results from sintering of experiment 70.

When the product was examined following the run, no ballooning was seen and the spheres had not turned a faded yellow color. A comparison of the product from experiment 70 is shown in Figure 30. By examining the figure, the non-heated microspheres are roughly 1000 µm in diameter. The sintered microspheres look to be ~500 µm. Both sets of microspheres are brittle and crumble easily. The spheres are solid though, setting the groundwork for future investigation.

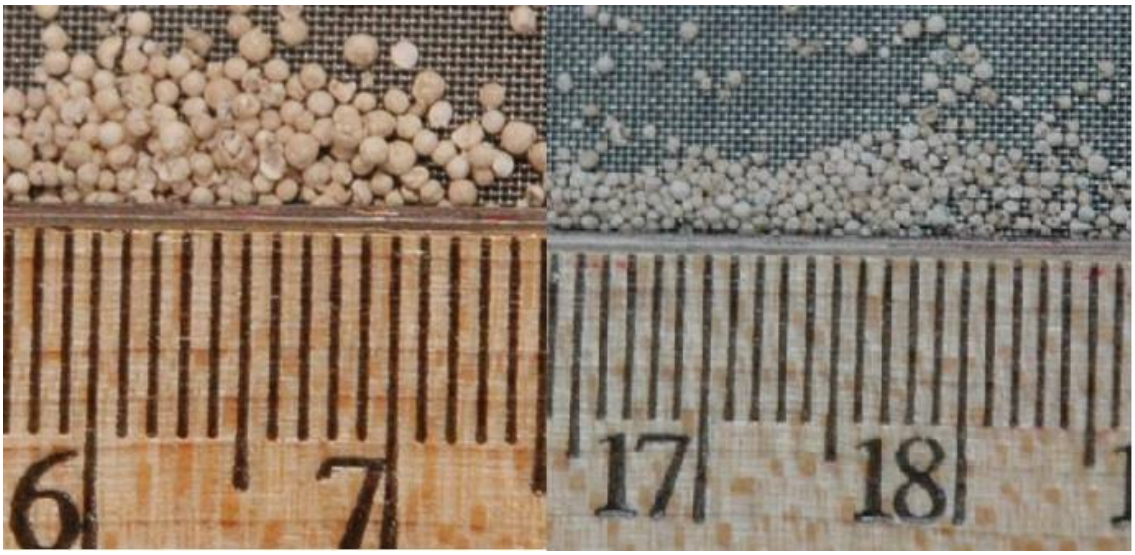

Figure 30. Photo of experiment 70 product; non-heated on left and sintered on right.

4.3.3 X-Ray Diffraction Analyses

To further characterize the sol-gel products from the experiments, X-Ray Diffraction (XRD) analysis was completed on several different products. The very first XRD spectra collected was for the poorly formed product from experiment 1. The gel that became caught in the funnel was washed in hexane and in a solution of 3 M

ammonium hydroxide. The XRD spectrum analysis (Figure 31) shows the product from experiment 1 was primarily cerium oxide or CeO_2. This indicates that even though the solid form was inadequate, the chemical form was exactly what was planned from the very first experiment.

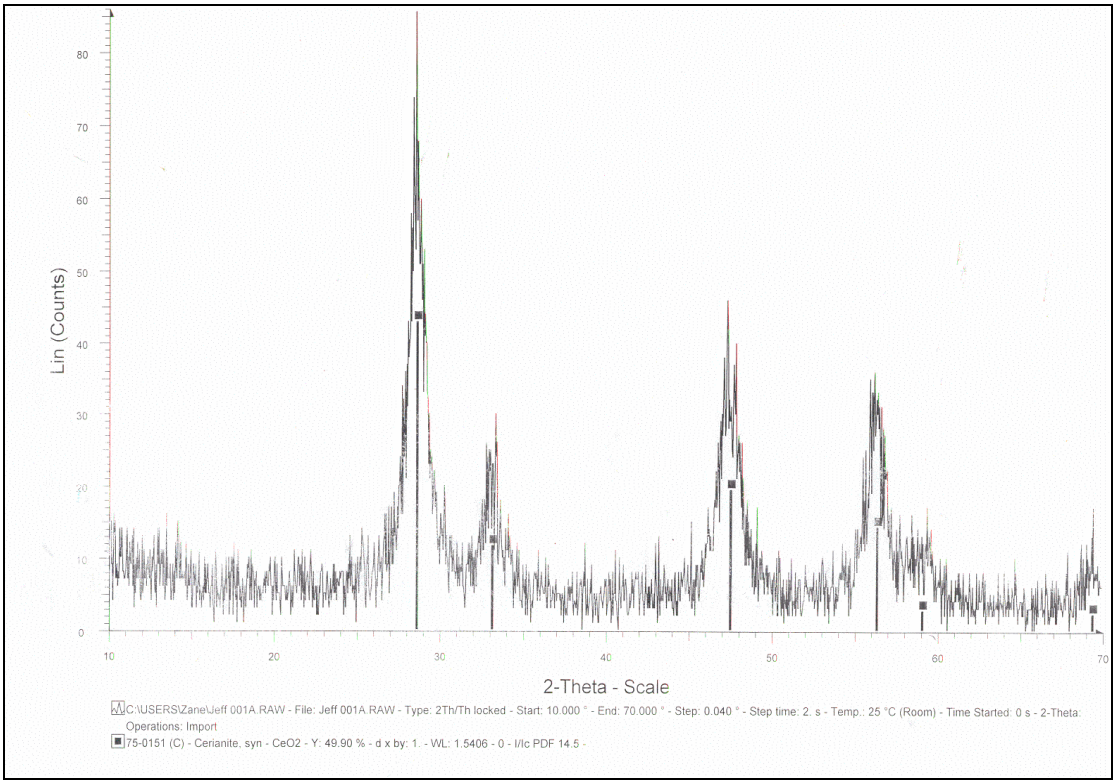

Figure 31. XRD analysis of experiment 1.

The second analysis was performed on the spheres produced during experiment 39. This experiment was the first to obtain solid quality spheres after drying; although only a hexane wash was used. In this case, the XRD analysis was unable to identify the product that was produced, as seen in Figure 32. This spectrum looks like an amorphous

collection of material, so this indicates that either the operator of the XRD system made a significant error during the test setup or the reaction was not complete. The first option is more likely since the reagents and conditions produced a product containing CeO_2 in every other case analyzed.

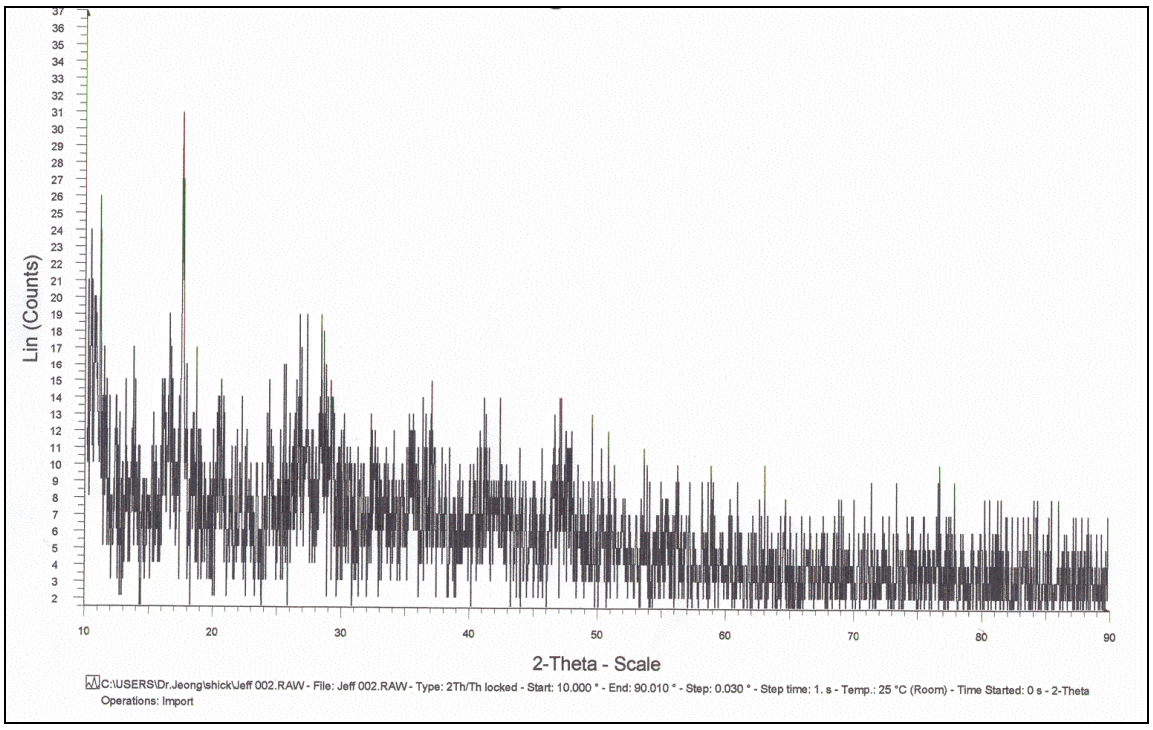

Figure 32. XRD analysis of experiment 39.

Two sets of analysis were performed on the spheres from experiment 56. This product was from the first batch of dried spheres that had been washed in hexane and then underwent a portion of the 3-stage washing process. These spheres, while brittle, were solid and did not dissolve or appear "popped" after drying. The analysis was able to determine that the microspheres were primarily cerium oxide along with an unknown

impurity material (Figure 33). The unknown impurity phase is evident from the minor peak at the 2θ value located between 11° and 12°.

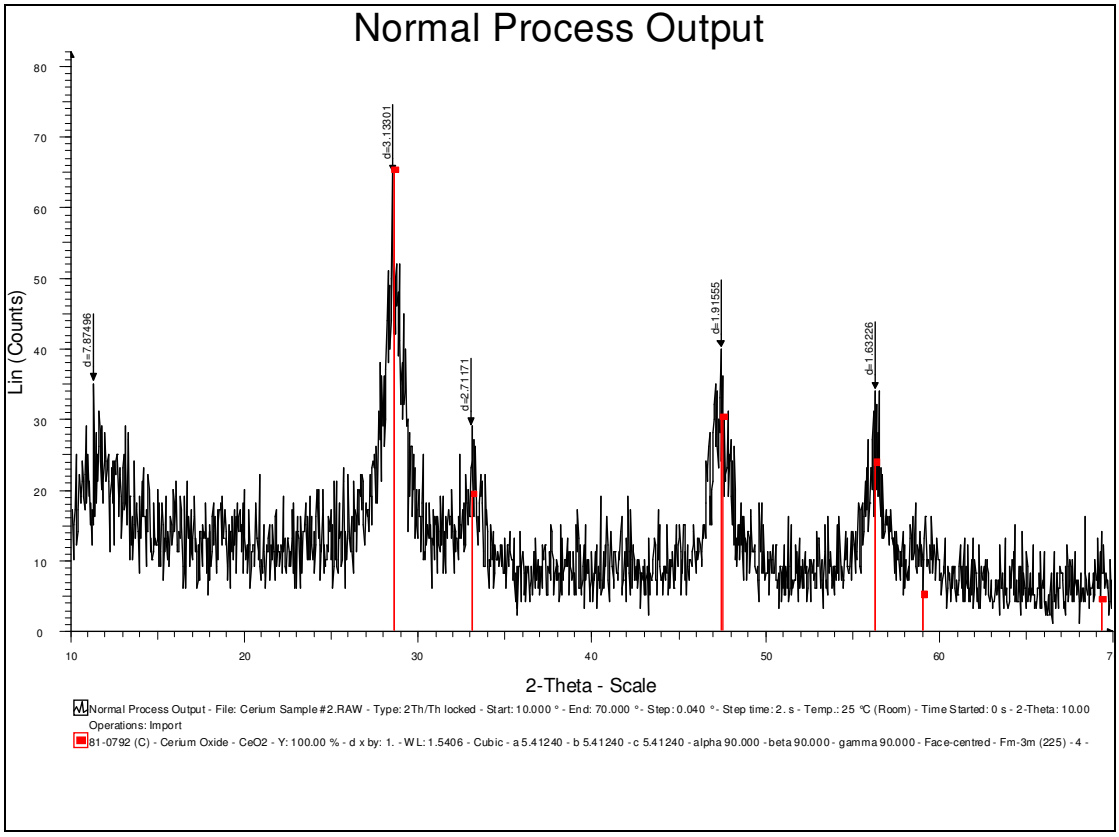

Figure 33. XRD analysis of non-heated product from experiment 56.

A second analysis was performed on material from experiment 56 using a sample that was meant to be heated to 1400°C in the STA to produce a reacted product for XRD analysis; however, at the exothermic range of 200°C the heating program was cancelled due to the evolution of vapor from the system exhaust and an automatic shutdown due to the transient. The product had swollen to several times its original size and turned black.

This was evidently due to the large volume of leftover chemicals within the spheres, as observed in experiment 56 in the previous section. The powder product was analyzed using XRD analysis; the product is shown in Figure 34 to be cerium oxide without the trace impurity phase noted above.

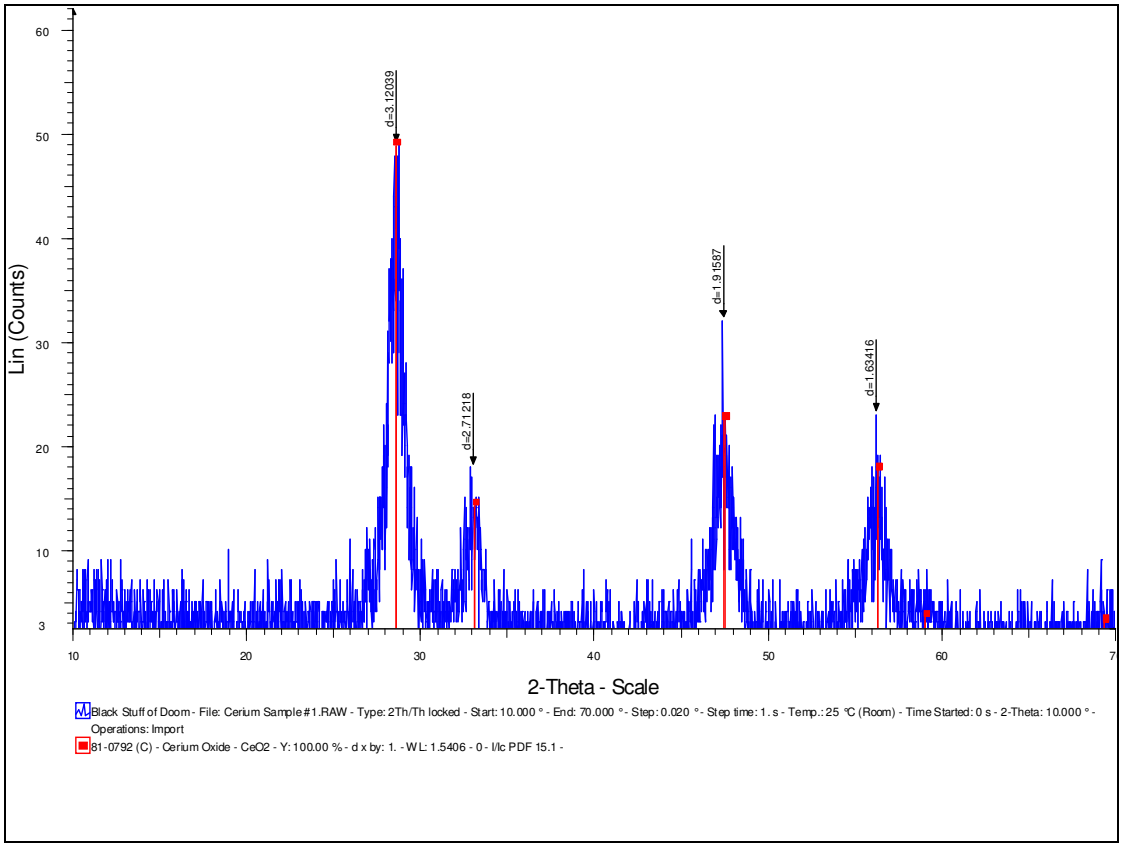

Figure 34. XRD analysis of heated product from experiment 56.

At the end of the process development tests, a number of XRD analyses were completed on spheres produced in experiment 69. The first analysis was carried out on "as-washed" spheres that had not been exposed to any heat treatment. The product was

identified as cerium oxide with an impurity material present as had happened with the unheated sample from experiment 56 (Figure 35). The analysis software selected guanidinium pentacarbonatocerate tetrahydrate as the most likely compound to match the impurity peak, but this was not confirmed by other methods. At the very least it seems that the impurity represents a cerium bearing organic compound that may be exothermically volatile at ~200°C.

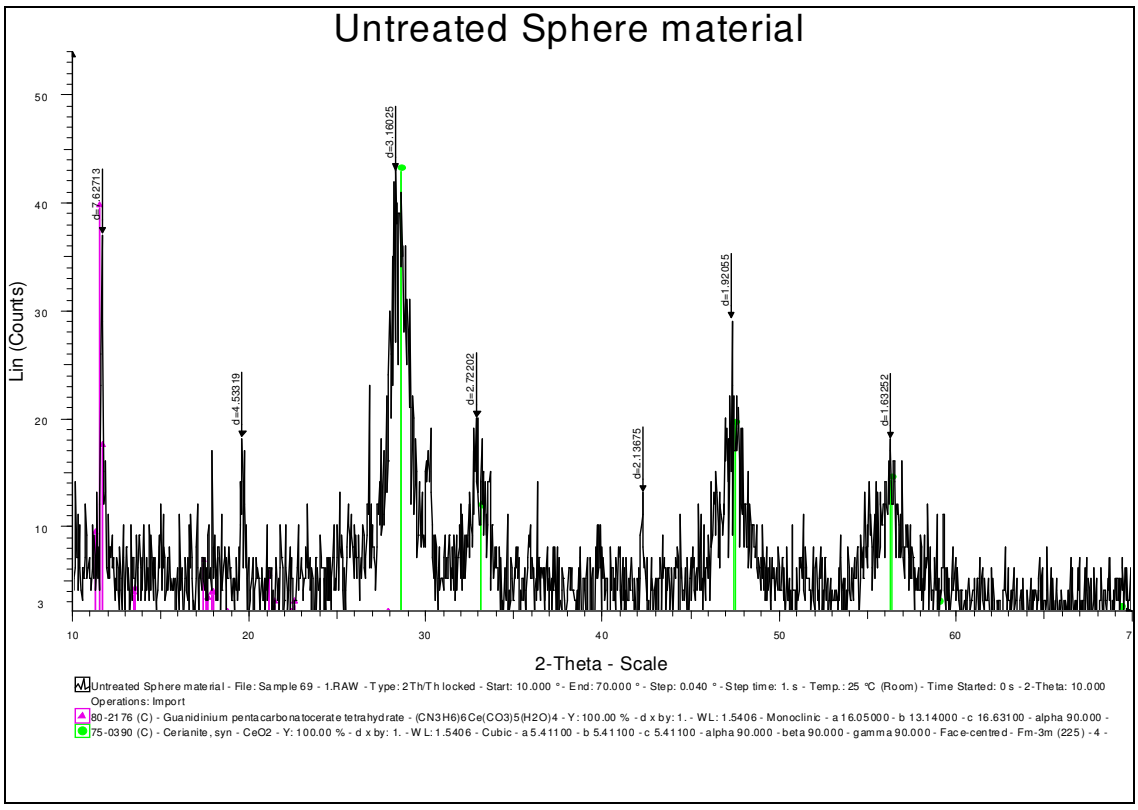

Figure 35. XRD analysis of non-heated product from experiment 69.

The second XRD analysis from experiment 69 was performed on spheres that had been heated to 175°C and then held at that temperature for two hours. The product

was identified as cerium oxide and there was no presence of the impurity that is present in unheated spheres, even though this sample was not taken up to the exothermic reaction temperature (Figure 36).

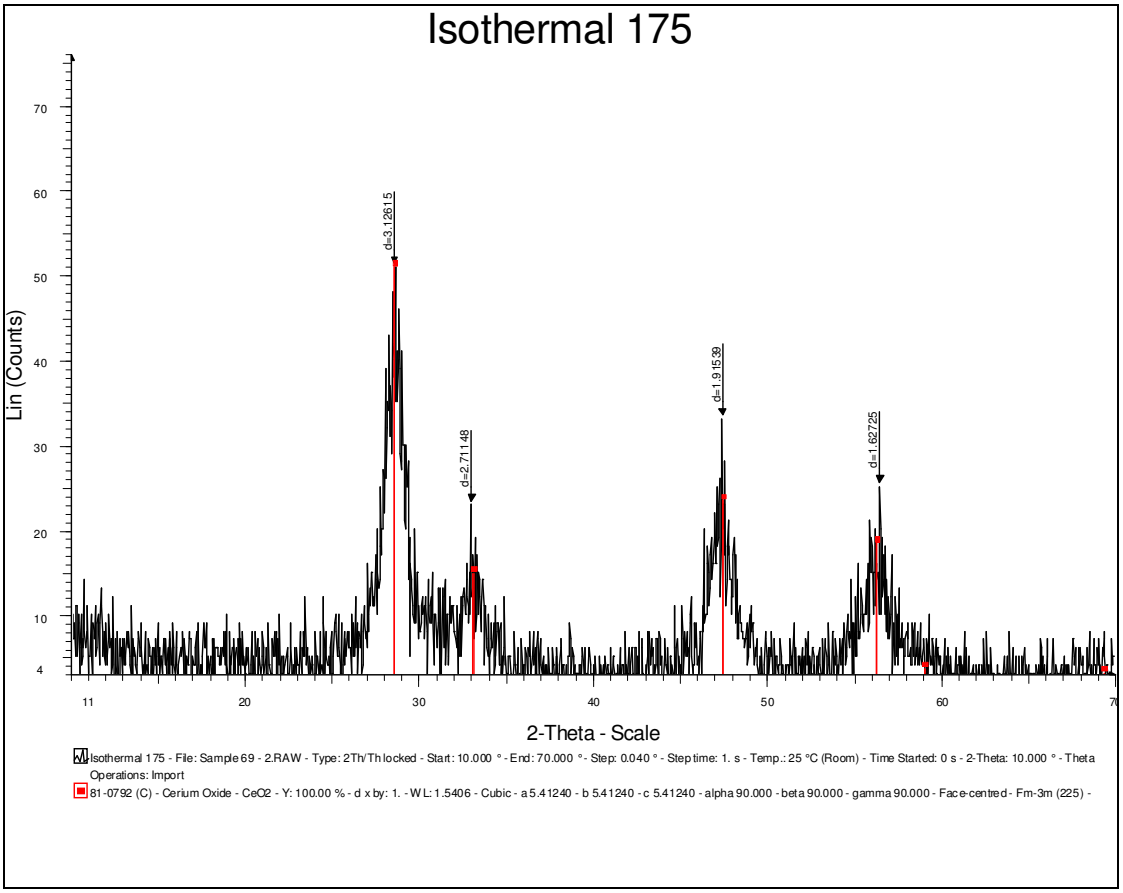

Figure 36. XRD analysis of experiment 69 product heated to 175°C.

The final XRD analysis on experiment 69 was performed on spheres that had been heated at 300°C for two hours. The product was clearly identified as only cerium oxide (Figure 37), which is the expected result after the impurity is removed during the heating process.

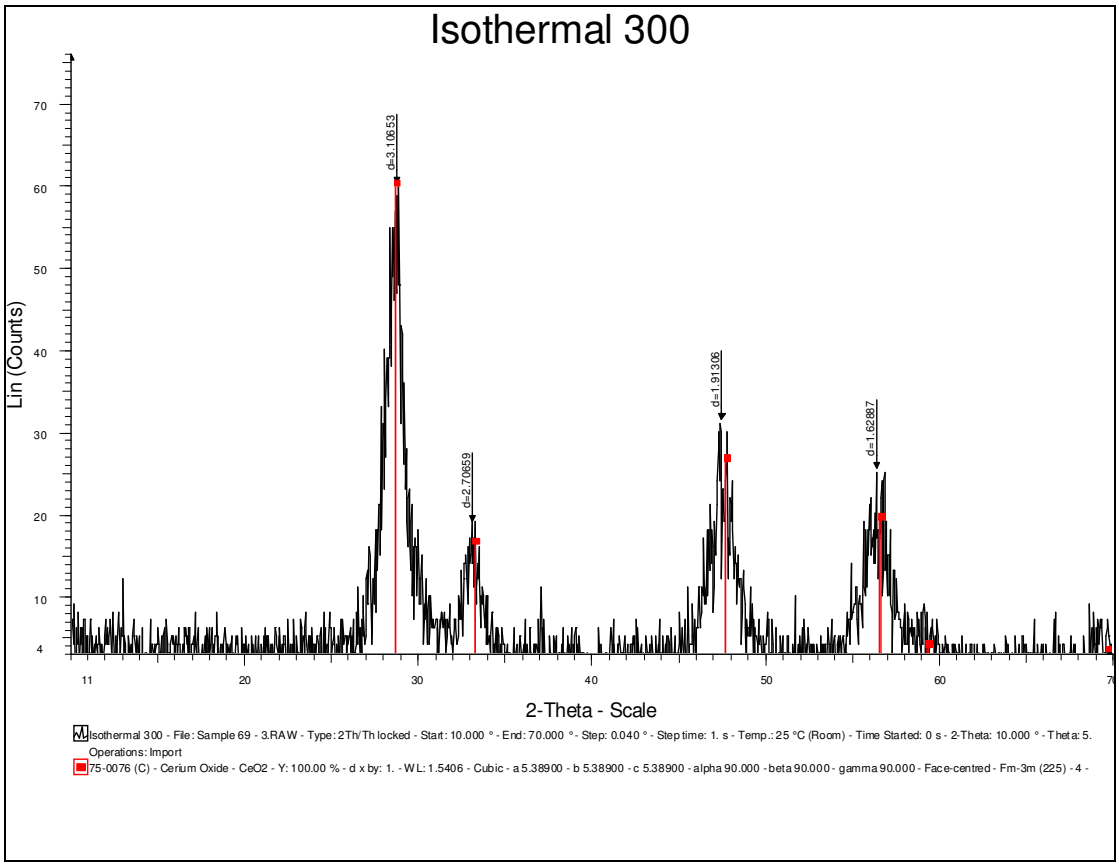

Figure 37. XRD analysis of experiment 69 product heated to 300^{o}.

Finally, two samples from experiment 70 were analyzed by XRD analysis. The first sample comprised as-washed spheres and the product was identified as cerium oxide containing two possible cerium-bearing organic compounds (Figure 38). The second sample was the sintered portion that had been heated to 1450^{o}C for four hours. This analysis, seen in Figure 39, showed that the sintered microspheres only contained cerium oxide.

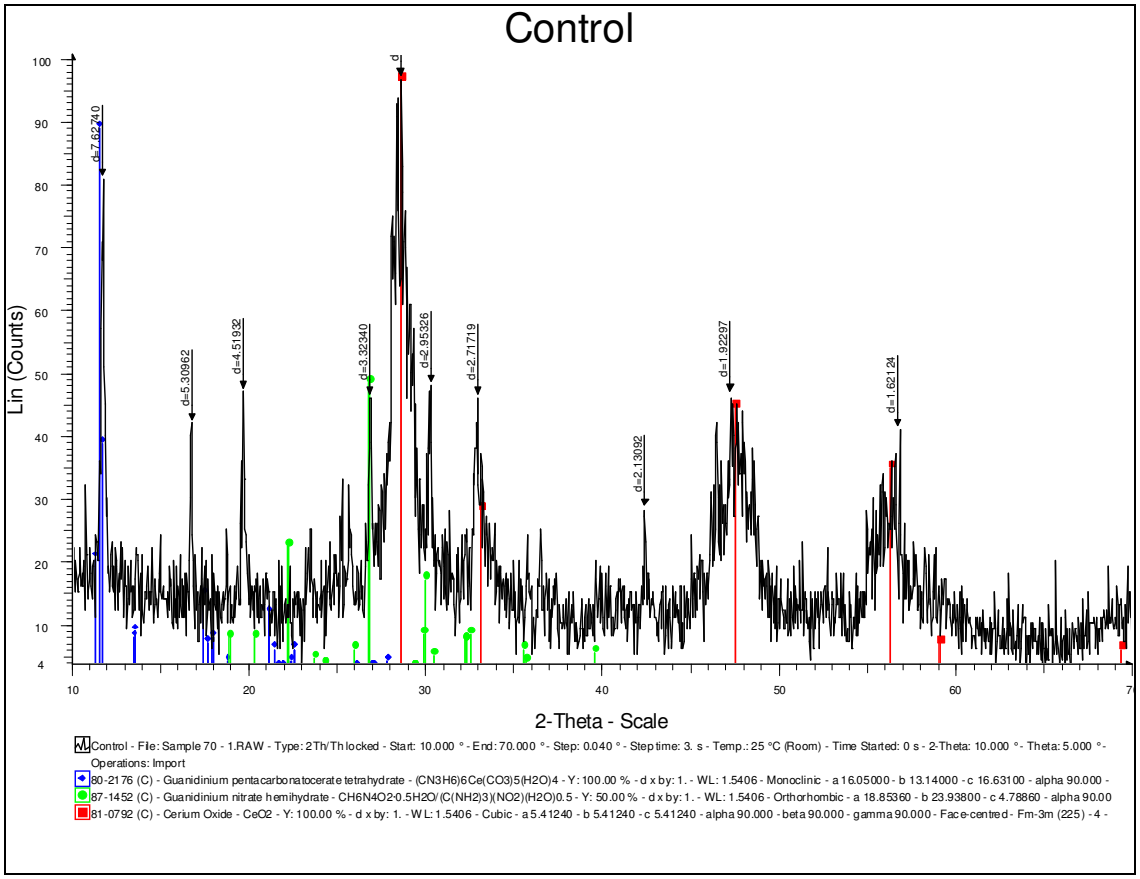

Figure 38. XRD analysis of non-heated product from experiment 70.

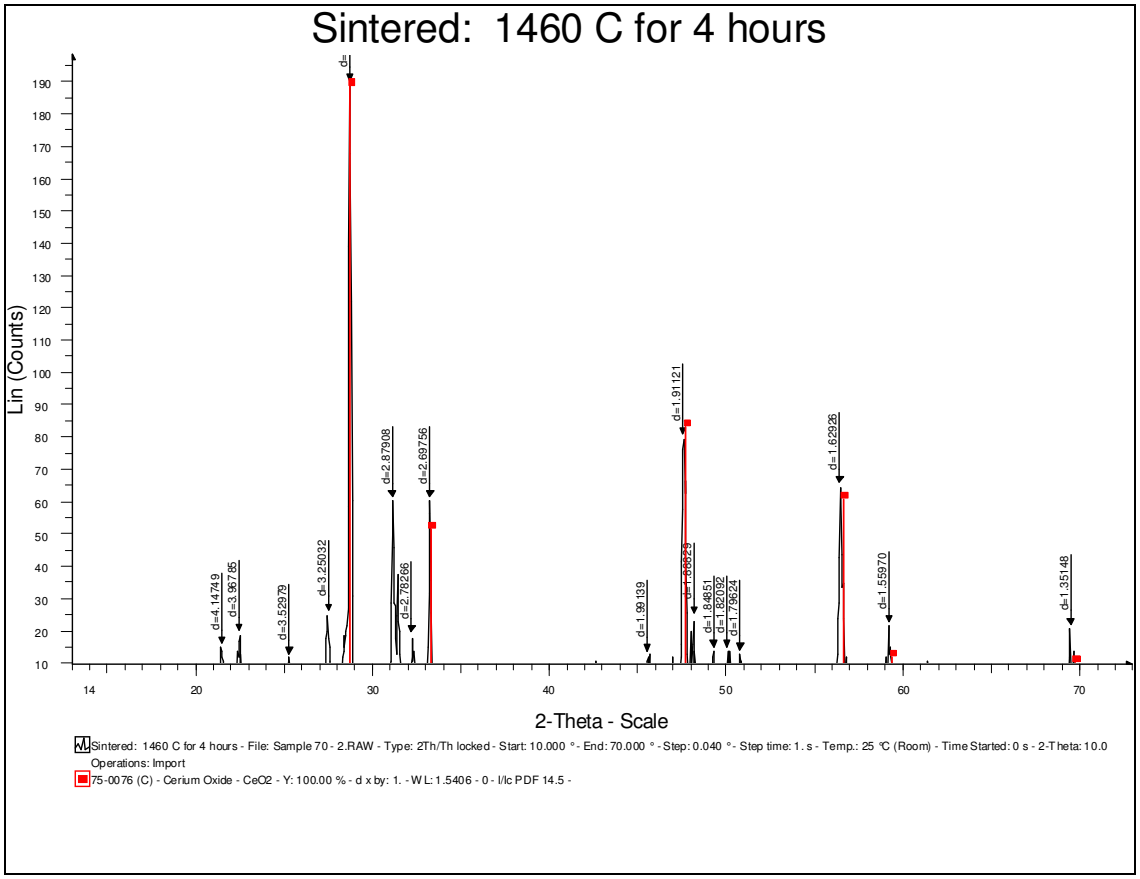

Figure 39. XRD analysis of sintered product from experiment 70.

5. DISCUSSION OF EXPERIMENTAL RESULTS

The experiments described in Section 4 were performed to develop and demonstrate a process designed to produce sintered cerium oxide microspheres by an internal gelation sol-gel process. The initial experiments were performed to gain an understanding into the sol-gel process itself and to establish the optimum equipment configuration within the experimental system. Changes were made to the apparatus as the experiments progressed and the later experiments were used to refine the concentration of the broth constituents and the washing procedure to produce the best usable spheres. A total of 70 experiments were completed, using varied concentrations, aging times, wash conditions, and other factors.

5.1 Experimental Observations

The early experimental runs, 1 through 12, all created a mass of unformed gel with few, if any microspheres present. The leading cause of the unformed material was the forced air system that was injecting the broth too rapidly from the broth storage chamber. Most of the forced air broth injections took place with pressures between 4 and 6 psi. While an actual flow measurement was never taken, it was much faster than the 0.15 mL/min used for the majority of the experiments after the syringe pump was installed. Another significant cause of unformed gelation in the early experiments was the absence of the gelation column that was introduced after experiment 9. The column provides a volume of low, non-turbulent flow for the broth spheres to form and to gel. The addition of the column also allowed the visual observation of the sphere gelation

reaction which enabled the operator to adjust the broth injection and silicone oil flow rates as needed.

The first observation after the first 12 experiments was that the composition of the broth may have been the cause behind the failure to create quality spheres. However, it eventually became evident the process procedures and equipment were the true cause of the problem. The 38 small scale tests (Section 4.2.1) revealed that the broth did indeed gel properly and that as the concentration of HMTA and urea is increased compared to the concentration of cerium nitrate, the internal gelation reaction is faster (Figure 10). The fact that the internal gelation reaction was occurring properly was further supported by the XRD data from experiment 1 that revealed that the unformed gel was still cerium oxide and not some other compound.

The small scale tests also showed that the outer shell of the gelled material became harder as the HMTA and urea to cerium nitrate ratio was increased. However, these tests did not evaluate the quality of the gel that was being produced. The increased ratio may have produced a faster gelling material, but later experiments have shown that an increased HMTA and urea level leads to cracked and hollow spheres before washing occurs. Due to the trend shown in those small scale tests, an increased HMTA and urea concentration was used for the next several experiments.

Another point of interest is that during the final small scale tests it was discovered that viable spheres could be produced if a syringe was manually used to inject the broth into the flowing oil rather than using the forced air system and a pressurized broth chamber. Therefore, these initial processing experiments proved to be

very informative. First, the gelation reaction was confirmed and the rate was quantified. Second, the true problem with the broth insertion rate was discovered and the transition was made to syringe injection.

The spheres produced using the manual injection syringe method (experiments 13 to 16) were of non-consistent size and many of the experiments had quantities of unformed gel due to inconsistencies in the manual injection speed. Also in this span, several different sized needles were used with mixed results. It was found that the 30 gauge needle easily clogged and the product was a layer of unformed gel. These experiments also used the same washing method, which consisted of a quick rinse in hexane and then a wash in 0.1 M ammonium hydroxide. When the product was placed into ammonium hydroxide, it appeared that many of the spheres dissolved. Due to the increased amount of HMTA and urea present within those experiments, it is possible that the ammonium hydroxide was causing the breakdown by interacting with unreacted reagents within the spheres.

Prior to experiment 17, the syringe pump was installed. The injection rate was varied slightly during experiment 18 while using a 28 gauge needle showing that the sphere size relied more on the size of the needle used rather than the injection rate over a small range of rates. Due to the inability of spheres to remain intact during washing, the concentration of HMTA and urea was decreased beginning in experiment 19, but the same washing procedure continued to be used. Also, starting at experiment 20 the needles were put in the freezer before the experiment run in an effort to prevent early

gelation. Until other process changes were made, freezing the needle before the experiment enabled more broth to be injected before clogging occurred.

As the amount of HMTA and urea within the broth was decreased, the quality of spheres upon removal from the oil increased. No longer were they cracked with a dark lavender color, instead they were an off white solid that was free flowing on top of the screen. In experiment 22 when the spheres were washed in the 0.1 M ammonium hydroxide solution, rather than breaking down as they had with a higher HMTA and urea concentration, the liquid instead only became cloudy, leaving many of the spheres intact. This indicated that the wash was removing reagents but the gelation process had matured farther than in previous experiments.

Some of the product from experiment 23 that was washed only in hexane was placed into an oven at 160^{o}C, after an undocumented amount of time the spheres had swollen, turned a shade of yellow, and had begun to smolder. The reason for this was likely an abundance of unreacted reagents on or within the spheres. The lack of complete gelation in the early experiments may account for the hollowness of the early product spheres and their breakdown upon washing in ammonium hydroxide.

Experiment 28 was the first test to approach the final 1.45 M cerium nitrate and 1.65 M HMTA and urea concentrations used for a large portion of the experiments. It was also the first test to produce spheres that did not appear hollow after drying; although they only received a hexane wash. Around this time it was noted that if any product began depositing in the syringe during injection, the entire run needed to be stopped, as any spheres produced beyond this point would be of the dark lavender

variety and not be of a good quality. Although the gelation reaction is temperature driven, once it begins it is autocatalytic and consumes the reagents wherever they are regardless of the temperature. Experiments 29 and 30 both provided a significant portion of quality spheres and it was noted that the proper broth concentration was likely to be between 1.64 to 1.68 M HMTA and urea and 1.43 to 1.46 M cerium nitrate. These concentrations bound the combination mentioned previously that consistently produced the best quality spheres. When the concentrations are dropped below these ranges, more unformed gel is produced with fewer spheres. This is likely due to the lack of ammonium being created from the decomposition of HMTA. This leads to some gelation, yet not enough to create a quality microsphere. When the experiments with a low HMTA concentration were washed in ammonium hydroxide, nearly all the unformed gel product dissolved away; leaving very little remaining. This is in contrast to the higher ratios where material does not dissolve, but the spheres are already cracked when removed from the oil reservoir.

After experiment 32 the significance of needle contamination became evident, and it was decided that syringes could not be reused after an experiment regardless of the amount of cleaning they undergo. Experiment 39 was the first of several runs where the spheres were only washed in hexane, skipping the ammonium hydroxide wash. The product from these experiments was solid and did not crack or crumble. Even after being set out to air dry and placed in a warm oven overnight they still maintained an oily, slightly wet feel. This could be a result of too short of a hexane wash or the

presence of unreacted reagents that were not removed with an ammonium hydroxide wash.

Experiment 42 was the final test to use a syringe that had been placed into a freezer before the run, and also the final test to experience early gelation in the syringe; which had been prevalent while using the frozen syringes. Earlier experiments, including those using the pressurized broth chamber, had experienced early gelation, but it was considered to be frozen broth. With this experiment, it became evident that this phenomenon was actually a premature manifestation of the gelation process, just at a slower speed than when introduced into the hot silicone oil. Experiment 42 was also the first to attempt to wash the spheres outside the stainless steel catch baskets and directly in beakers. A 3 M solution of ammonium hydroxide was used for an undocumented amount of time before the spheres were placed onto a section of mesh screen to dry. The resulting product had a chalky appearance, a condition that continued throughout the rest of the experiment runs.

After several attempts at washing with varying solutions of ammonium hydroxide, the standard wash procedure developed at Oak Ridge National Laboratory for UO_2 gelation spheres was implemented after a further literature review. The first stage of the wash consists of 50% isopropyl alcohol and 50% 1.5 M ammonium hydroxide. Stage two involves a solution of 0.5 M ammonium hydroxide, and the final stage is 75% isopropyl alcohol [13]. The ability to do multiple stage washing was enabled by the introduction of baskets with a bottom made from 40 x 40 stainless steel mesh. The body of the baskets remained 80 x 80 mesh until experiment 63, when the entire basket

became 40 x 40 mesh. Initially each step was performed for 50 minutes; however, that was increased to 60 minutes for most of the following experiments.

The first observation from the new multi-stage wash procedure was that the washed spheres did not stick together or to the mesh after washing. The inclusion of isopropyl alcohol in the wash process is the likely reason for this. During the first washing stage any unformed gel present dissolves and leaves only the product spheres behind. Even if no unformed gel is present, some material is removed from the spheres, evidenced visually by the wash solution becoming cloudy during the process. This is likely to be unreacted reagents on the outer surface of the spheres. During the second wash not as much material is removed from the spheres, but they begin a noticeable color change. By the end of the second wash, most of the spheres will have gone from a white color to a darker white with a yellow hue. Also, some of the spheres agglomerate together and some are more likely to become attached to the bottom of the basket or the side wall. No color change was observed during the third wash. However, spheres that stick to each other in the second wash tend to come apart during the third wash. In experiment 62 a magnetic stirrer was implemented during the wash process. It was used intermittently throughout the remaining experiments as various techniques were used in an attempt to elevate the basket above the spinning bar.

From experiment 50 through 59, all materials were allowed to age for a varying amount of time, washed in hexane, then washed using the Oak Ridge 3-stage washing process. When finished, nearly all of the spheres looked to be solid and were not cracked or crumbling. After being allowed to dry, all of the spheres exhibited the dry,

chalky appearance noted above. It was thought that the concentration of active material may have been too high within the broth, so beginning with experiment 60, water was added to the broth solution in an effort to dilute it.

The ratio of HMTA and urea to cerium nitrate was kept consistent throughout most of the next several experiments; just the amount of the diluting water added was varied. Experiment 63 showed that the addition of too much water led to a product that consisted almost entirely of unformed gel. That solution was accidentally diluted to 1.35 M HMTA and urea and 1.05 M cerium nitrate. The resulting product of unformed gel dissolved during the wash process. Experiments 64 and 66, also with diluted broths, obtained no better spheres than those that had not been diluted. From these experiments it was determined that the strength of the solutions was not responsible for the cracked spheres produced during drying.

The final two experiments run, 69 and 70, raised the temperature of the oil flowing through the system and kept the basket elevated above the oil reservoir until the aging process was completed. The temperature was raised due to the variations seen in the gelation speed with different oil temperatures. At lower temperatures, the gelation process did not occur until near the bottom of the column. These tests were performed to determine if higher quality spheres could be produced if the oil temperature was raised. The spheres produced from these runs were solid, although brittle. At this point, the process development was concluded and the final characterization tests were completed. The product from these two experiments provided the majority of the materials analyzed in Section 4.3.

5.2 Product Characterization

Products from experiments 1, 39, 56, 69 and 70 were analyzed using TGA, DSC and XRD analysis methods. The product from experiment 1 was confirmed by X-ray diffraction to be cerium oxide (Fig. 31); the ceramic material that was the object of these experiments. Since the form of the cerium oxide product was not spherical, but rather an amorphous blob, the remaining work was focused on generating the desired spherical product (It should be noted as well that approximately 3 months elapsed before the product of experiment 1 underwent XRD analysis). Throughout all of the tests, it is apparent that the internal gelation product was primarily cerium oxide. "Extra" peaks were observed in the unwashed, partially washed, and thermally-processed samples indicating that some leftover reagents or rogue compounds are always present in the washed spheres.

The spheres formed in experiment 39 were the next to undergo analysis. Through XRD, the form of the product was not able to be identified (Fig. 32). After aging, the spheres were washed in hexane and did not undergo an ammonium hydroxide wash. Unreacted product from the gelation process, leftover hexane, or unremoved silicone oil could all be responsible for the inability to identify the product. The spectrum indicated that the product was an apparently amorphous collection of material. As noted, this indicates that either the operator of the XRD system made a significant error during the test setup or the reaction was not complete. The first option is more likely since the reagents and conditions produced a product containing a significant quantity of CeO_2 in every other sample that was analyzed.

Spheres produced in experiment 56 underwent TGA, DSC, and XRD. The portion not undergoing heat treatment was identified through XRD as being partially cerium oxide with other material present (Fig. 33). The spheres from experiment 56 underwent a hexane wash and the first step of the 3-stage wash until the basket failed. The DSC/TGA results indicated that a volatile species was being liberated at ~200^{o}C (Fig. 23). It is suspected that this represents the evaporation of leftover reagents that were not removed by washing.

The product from experiment 69 was split into several small samples before undergoing the various analysis techniques. Recall that experiments 69 and 70 were the final production tests that produced the best available microspheres. A small portion was heated to 500^{o}C for TGA and DSC evaluation. The exothermic reaction observed in experiment 56 was again observed, but the magnitude of the reaction was significantly reduced (compare Figs. 23 and 24). The spheres from experiment 69 were washed with the complete washing process, as opposed to experiment 56 that only went through the first stage. By going through the full wash process, more unreacted product was removed from the spheres. The same results were seen for a larger sample of spheres taken above the 200^{o}C reaction point. The product turned a pale yellow color and remained intact. The XRD results from the three samples from experiment 69 (Figs. 35 to 37) show that even being heated below 200^{o}C is enough to remove the impurity phase, leaving the cerium oxide as the only observable phase. And although Figure 35 shows a strong peak matching guanidinium pentacarbonatocerate tetrahydrate, the data was not conclusive enough to identify that species as the impurity phase.

Product from experiment 70, produced using the same conditions as experiment 69, was taken up to over 1400°C to simulate sintering. The portion undergoing just TGA underwent the typical mass drop around 200°C with minimal mass loss above that point (Fig. 29). The final product was a slightly smaller sphere caused by densification through sintering (Fig. 30). The product would not be usable for pressing due to the cracking observed, but it was able to survive the temperatures needed for the sintering process without the destructive reactions from remnant reagents. If the microspheres sintered in experiment 70 were to be used in the production of cermet fuels, they would not be able to withstand the pressures involved in the pressing process. Even after sintering, the microspheres were brittle and crumbled under very little pressure.

6. SUMMARY AND RECOMMENDATIONS

Seventy process development experiments were performed to establish a system to produce cerium oxide microspheres through internal gelation. To accomplish this task, various process variables were altered, including broth composition, oil temperature, injection rate, and wash steps and times. Through the techniques investigated in this research, it is possible to produce cerium oxide microspheres that are solid, but brittle, and are able to withstand washing and sintering.

The following are the observations and results obtained from the experiments performed:

1. Increased concentrations of HMTA and urea lead to faster gelation, but the quality of the spheres is decreased. Results of the small scale tests show a 2:1 ratio of HMTA and urea to cerium nitrate produces the fastest gelling material for the conditions studied. However, experiments performed with this composition produced spheres that were cracked when removed from the oil.
2. Spheres of the highest quality came from a broth composed of 1.45 M cerium nitrate and 1.65 M HMTA and urea. When not washed in ammonium hydroxide, the product spheres were solid and did not crack or crumble while drying. Cracking occurs when undergoing the full wash process, but the produced spheres were the best produced in this study.
3. Introduction of the gelation column and syringe pump was a key to the production of microspheres. The gelation column created a volume of low

disturbance and low flow for the initial structure of the spheres to be formed. It also allowed real time correction to the injection speed as the spheres could be observed flowing through the column. The syringe pump allowed the broth to be injected slowly enough for microspheres to be produced.

4. Contamination became a serious issue when working with the optimum broth solution. Due to this, new syringes were used for every experiment run and the needles were thoroughly washed to remove product from previous runs. Introduction of any foreign material may lead to the needle clogging and early gelation in the syringe.

The following are recommendations for any future research into this area:

1. Only a small investigation of sphere production at greater than 100^{o}C was completed. Further analysis may show a higher temperature will allow production of spheres that are not cracked during the drying process.
2. The gelation column used was originally to be longer, but it was cracked during the installation process and had to be shortened. A column of greater length would allow the spheres a longer time in the low flow region to provide superior gelation.
3. The final experiments were completed using baskets of 40 x 40 mesh and washed by placing these baskets into a beaker. Attempts were made to use a magnetic stirrer to flow the wash over the baskets, but the experimental setup was unstable. By designing a better washing stand, more waste may be removed from the spheres by a flowing wash.

4. Further analysis is needed of the produced spheres before and after sintering to determine particle size and density. Densification should occur during the sintering process, it is desired to know the extent.
5. The next stage of this research should include the extension to mixed oxides, especially uranium-cerium oxides.

REFERENCES

[1] G.J. Suppes, T.S. Storvick, Sustainable Nuclear Power, Academic Press, New York, 2007.

[2] I. Hore-Lacy, Nuclear Energy in the 21st Century, Academic Press, New York, 2007.

[3] Yucca Mountain Repository License Application, DOE/RW-0573 (2008).

[4] A.J. Parkison, thesis, Texas A&M University, College Station, 2008.

[5] A.R. Totemeier, thesis, Purdue University, West Lafayette, IN, 2006.

[6] S.M. McDeavitt, A. Parkison, A.R. Totemeier, J.J. Wegener, Mater. Sci. Forum. 561-565 (2007) 1733-1736.

[7] S.M. McDeavitt, Development of an Engineered Product Storage Concept for the UREX+1 Combined Transuranic/Lanthanide Product Streams, Quarterly Progress Report, July 1, 2005.

[8] J.L. Collins, R.D. Hunt, G.D. Del Cul, D.F. Williams, Production of Depleted UO_2 Kernels for the Advanced Gas-Cooled Reactor Program For Use in TRISO Coating Development, ORNL/TM-2004/123 (2004).

[9] P. Naefe, E. Zimmer, Nucl. Tech. 42 (1979) 163-71.

[10] J.L. Collins, M.H. Lloyd, R.L. Fellows, Radiochim. Acta. 42 (1987) 121-134.

[11] J.L. Collins, Experimental Methodology for Determining Optimum Process Parameters for Production of Hydrous Metal Oxides by Internal Gelation, ORNL/TM-2005/102 (2005).

[12] V.N. Vaidya, S.K. MukerJee, J.K. Joshi, R.V. Kamat, D.D. Sood, J. Nucl. Mater. 148 (1987) 324-31.

[13] P.A. Haas, J.M. Begovich, A.D. Ryon, J.S. Vavruska, Ind. Eng. Chem. Prod. Res. Dev. 19 (1980) 459-67.

[14] R.D. Hunt, J.L. Collins, Radiochim. Acta. 92 (2004) 909-15.

[15] J.L. Collins, J.S. Watson, Economic Evaluation for the Production of Sorbents and Catalysts Derived from Hydrous Titanium Oxide Microspheres Prepared by the HMTA Internal Gelation Process, ORNL/TM-1999/212 (2000).

[16] J.C. Marra, A.D. Cozzi, R.A. Pierce, J.M. Pareizs, Cerium as a Surrogate in the Plutonium Immobilized Form, DE-AC09-96SR18500.

APPENDIX A

EXPERIMENTAL CONDITIONS AND RESULTS

Experiment 1

HMTA / Urea:	1.68 M	Cerium Nitrate:	1.3 M	Flowing Oil:	90 C
Needle:	18 ga	Air Pressure:	Undocumented	Aging Time:	10 min

Wash: Undocumented

Product Result: Solid yellow crust at bottom of oil reservoir; material in catch funnel never fully gels

Notes: Experiment used Neslab constant temperature bath and funnel for catch basket

Experiment 2

HMTA / Urea:	1.68 M	Cerium Nitrate:	1.3 M	Flowing Oil:	90 C
Needle:	18 ga	Air Pressure:	4 psi	Aging Time:	Undocumented

Wash: Undocumented

Product Result: Unformed gel product filling catch basket

Notes: Pressure increased to 4.5 psi during run; used large oil reservoir

Experiment 3

HMTA / Urea:	1.68 M	Cerium Nitrate:	1.3 M	Flowing Oil:	90 C
Needle:	18 ga	Air Pressure:	4 psi	Aging Time:	Undocumented

Wash: Hexane and Ammonium Hydroxide

Product Result: Unformed gel product filling catch basket

Notes: Pressure started at 4 psi, reduced during run to obtain lower flow rate

Experiment 4

HMTA / Urea:	1.68 M	Cerium Nitrate:	1.3 M	Flowing Oil:	90 C
Needle:	18 ga	Air Pressure:	3.75 psi	Aging Time:	Undocumented
Wash:	Hexane and Ammonium Hydroxide				
Product Result:	Some small sphere "flecks" in unformed gel				
Notes:	Pressure increased up to 4 psi before needle blockage				

Experiment 5

HMTA / Urea:	1.68 M	Cerium Nitrate:	1.3 M	Flowing Oil:	90 C
Needle:	18 ga	Air Pressure:	4 psi	Aging Time:	Undocumented
Wash:	Hexane and Ammonium Hydroxide				
Product Result:	Small amounts of white "specks" in output stream before injection flow stops				
Notes:	Early gelation around points of metal in injection system stops run				

Experiment 6

HMTA / Urea:	1.68 M	Cerium Nitrate:	1.3 M	Flowing Oil:	90 C
Needle:	18 ga	Air Pressure:	4 psi	Aging Time:	Undocumented
Wash:	Hexane and Ammonium Hydroxide				
Product Result:	Mixture of unformed gel with some small spheres				
Notes:	Running start used; broth flowing out of tip of needle when inserted into flowing oil				

Experiment	7				
HMTA / Urea:	1.68 M	Cerium Nitrate:	1.3 M	Flowing Oil:	90 C
Needle:	18 ga	Air Pressure:	3.75 psi	Aging Time:	Undocumented
Wash:	Hexane and Ammonium Hydroxide				
Product Result:	Appears more as film than unformed gel or spheres				
Notes:	Running start used again				

Experiment	8				
HMTA / Urea:	1.92 M	Cerium Nitrate:	1.2 M	Flowing Oil:	90 C
Needle:	18 ga	Air Pressure:	5 psi	Aging Time:	Undocumented
Wash:	Hexane and Ammonium Hydroxide				
Product Result:	Some very large spheres and unformed gel				
Notes:	First experiment with altered chemistry				

Experiment	9				
HMTA / Urea:	2.13 M	Cerium Nitrate:	1 M	Flowing Oil:	90 C
Needle:	18 ga	Air Pressure:	4 psi	Aging Time:	Undocumented
Wash:	---				
Product Result:	Oil backed up into system; experiment stopped				
Notes:	Slime like surface created when pressure increased to counter oil back flow				

Experiment 10

HMTA / Urea:	1.92 M	Cerium Nitrate:	1.2 M	Flowing Oil:	90 C
Needle:	18 ga	Air Pressure:	4 psi	Aging Time:	Undocumented

Wash: Hexane and Ammonium Hydroxide

Product Result: Mass of unformed gel

Notes: First experiment with gelation column; still using forced air injection

Experiment 11

HMTA / Urea:	1.92 M	Cerium Nitrate:	1.2 M	Flowing Oil:	90 C
Needle:	18 ga	Air Pressure:	4 psi	Aging Time:	Undocumented

Wash: Hexane and 3 M Ammonium Hydroxide

Product Result: Some spheres seen falling through column, although not all gelling; washed product has some spheres and unformed gel

Notes: Early gelation occurs around ball valve area of broth chamber

Experiment 12

HMTA / Urea:	1.6 M	Cerium Nitrate:	1.5 M	Flowing Oil:	90 C
Needle:	18 ga	Air Pressure:	< 0.5 psi	Aging Time:	Undocumented

Wash: Hexane and 3 M Ammonium Hydroxide

Product Result: Unformed gel with some spheres within

Notes: With flow only from the air valve turned off still injecting at too high of a rate

Experiment 13

HMTA / Urea:	2.13 M	Cerium Nitrate:	1 M	Flowing Oil:	100 C
Needle:	18 ga	Manual Syringe Injection		Aging Time:	Undocumented

Wash: Hexane and 0.1 M Ammonium Hydroxide

Product Result: Many spheres, although unformed gel by manual injection

Notes: Following small scale tests, learned can create spheres by using syringe manually

Experiment 14

HMTA / Urea:	2.13 M	Cerium Nitrate:	1 M	Flowing Oil:	100 C
Needle:	30 ga	Manual Syringe Injection		Aging Time:	Undocumented

Wash: ---

Product Result: Needle clogged within seconds; only unformed gel produced

Notes: 30 gauge needle is much to small to inject spheres without clogging

Experiment 15

HMTA / Urea:	2.13 M	Cerium Nitrate:	1 M	Flowing Oil:	100 C
Needle:	24 ga	Manual Syringe Injection		Aging Time:	Undocumented

Wash: Hexane, 0.1 M Ammonium Hydroxide, and Water

Product Result: Spheres produced during run; placed in 80 C oven overnight, seem to have "melted"

Notes: Rough measurements on sphere sizes show to be between 560 and 690 µm

Experiment	16				
HMTA / Urea:	2.13 M	Cerium Nitrate:	1 M	Flowing Oil:	100 C
Needle:	24 ga (f)	Manual Syringe Injection		Aging Time:	Undocumented
Wash:	Hexane, 0.1 M Ammonium Hydroxide, and Water				
Product Result:	Spheres produced during run; placed in 80 C oven overnight, seem to have "melted"				
Notes:	First run with frozen needle; appeared to be able to inject much more				

Experiment	17				
HMTA / Urea:	2.13 M	Cerium Nitrate:	1 M	Flowing Oil:	100 C
Needle:	26 ga	Injection Rate:	0.2 mL/min	Aging Time:	Undocumented
Wash:	Hexane, 0.1 M Ammonium Hydroxide, and Water				
Product Result:	Many small spheres produced during run; product seems "popped" or "melted"				
Notes:	First experiment with syringe pump; injection rate variable removed				

Experiment	18				
HMTA / Urea:	2.13 M	Cerium Nitrate:	1 M	Flowing Oil:	100 C
Needle:	26 ga	Injection Rate:	Varied	Aging Time:	Undocumented
Wash:	Hexane, 0.1 M Ammonium Hydroxide, and Water				
Product Result:	Solid spheres after aging; placed in 40 C oven to dry; appear "popped" or "melted"				
Notes:	Variation of injection rate over a small range does not seem to alter sphere size				

Experiment 19

HMTA / Urea:	1.92 M	Cerium Nitrate:	1.2 M	Flowing Oil:	100 C
Needle:	26 ga	Injection Rate:	0.2 mL/min	Aging Time:	20 min

Wash: Hexane, 0.1 M Ammonium Hydroxide, and Water

Product Result: Spheres appear good after washing, some appear "melted" after drying in oven overnight

Notes: Under scope some of the spheres appear not hollow

Experiment 20

HMTA / Urea:	1.78 M	Cerium Nitrate:	1.33 M	Flowing Oil:	100 C
Needle:	26 ga (f)	Injection Rate:	0.2 mL/min	Aging Time:	15 min

Wash: Hexane and 0.1 M Ammonium Hydroxide

Product Result: Free flowing after hexane wash; Ammonium Hydroxide made them stick in place; broken down next day

Notes: Continuing decreasing HMTA and urea concentration; some spheres lost to hole in basket

Experiment 21

HMTA / Urea:	1.68 M	Cerium Nitrate:	1.43 M	Flowing Oil:	100 C
Needle:	24 ga	Injection Rate:	0.1 mL/min	Aging Time:	15 min

Wash: Hexane and 0.1 M Ammonium Hydroxide

Product Result: Solid product after aging and hexane wash; following Ammonium Hydroxide and aging appear "melted"

Notes: Further decreasing of HMTA and urea concentration

Experiment 22

HMTA / Urea:	1.78 M	Cerium Nitrate:	1.33 M	Flowing Oil:	100 C
Needle:	24 ga (f)	Injection Rate:	0.1 mL/min	Aging Time:	30 min

Wash: Hexane and 0.1 M Ammonium Hydroxide

Product Result: Solid spheres out of aging, once washed in Ammonium Hydroxide becomes cloudy with "crud" forming

Notes: Needle clogged after 1.3 mL injected, 22 ga used for remainder

Experiment 23

HMTA / Urea:	1.78 M	Cerium Nitrate:	1.33 M	Flowing Oil:	100 C
Needle:	18 ga	Injection Rate:	0.7 mL/min	Aging Time:	30 min

Wash: Hexane

Product Result: Non-melted spheres after drying; some appear hollow

Notes: Seeing effects of not washing with Ammonium Hydroxide

Experiment 24

HMTA / Urea:	1.68 M	Cerium Nitrate:	1.3 M	Flowing Oil:	100 C
Needle:	24 ga (f)	Injection Rate:	0.2 mL/min	Aging Time:	45 min

Wash: Hexane and Water

Product Result: Free flowing spheres during hexane wash; breaking down when in contact with water

Notes: Needle clogged after 1.6 mL injected, 26 ga used for remainder

Experiment	25				
HMTA / Urea:	1.6 M	Cerium Nitrate:	1.5 M	Flowing Oil:	100 C
Needle:	26 ga (f)	Injection Rate:	0.2 mL/min	Aging Time:	---
Wash:	---				
Product Result:	Needle clogged almost immediately; experiment scrapped				
Notes:	After needle clogged, entire syringe began to gel				

Experiment	26				
HMTA / Urea:	1.92 M	Cerium Nitrate:	1.2 M	Flowing Oil:	110 C
Needle:	24 ga (f)	Injection Rate:	0.2 mL/min	Aging Time:	30 min
Wash:	Hexane and Water				
Product Result:	Many small spheres and some unformed gel; appear hollow when dried				
Notes:	Increased amount of HMTA and urea				

Experiment	27				
HMTA / Urea:	1.78 M	Cerium Nitrate:	1.33 M	Flowing Oil:	110 C
Needle:	24 ga (f)	Injection Rate:	---	Aging Time:	---
Wash:	---				
Product Result:	Sediment formed as soon as loaded into syringe; experiment scrapped				
Notes:	Realized had been using same syringe for all experiments				

Experiment 28

HMTA / Urea:	1.6 M	Cerium Nitrate:	1.5 M	Flowing Oil:	100 C
Needle:	22 ga (f)	Injection Rate:	0.2 mL/min	Aging Time:	30 min

Wash: Hexane

Product Result: Excess of unformed gel; upon drying appears many are not hollow

Notes: New syringes used and made sure that broth is chilled thoroughly

Experiment 29

HMTA / Urea:	1.64 M	Cerium Nitrate:	1.46 M	Flowing Oil:	100 C
Needle:	22 ga (f)	Injection Rate:	0.2 mL/min	Aging Time:	120 min

Wash: Undocumented

Product Result: Two different color products; white / light pink that is solid and purple / lavender that is cracked

Notes: Several attempts required to get experiment set up, end up pouring broth into syringe through the top rather than drawing in through the needle

Experiment 30

HMTA / Urea:	1.68 M	Cerium Nitrate:	1.3 M	Flowing Oil:	100 C
Needle:	22 ga (f)	Injection Rate:	0.2 mL/min	Aging Time:	30 min

Wash: Hexane

Product Result: Majority of spheres are lighter colored; next day white product is not hollow while darker is dried and cracked

Notes: Paid extra attention to make sure no early gelation occurring in syringe

Experiment 31

HMTA / Urea:	1.62 M	Cerium Nitrate:	1.48 M	Flowing Oil:	100 C
Needle:	22 ga (f)	Injection Rate:	0.2 mL/min	Aging Time:	30 min

Wash: Hexane and 0.1 M Ammonium Hydroxide

Product Result: Spheres with unformed gel connecting; during washing unformed gel dissolves leaving spheres only

Notes Extra effort put into removing contamination from system components

Experiment 32

HMTA / Urea:	1.68 M	Cerium Nitrate:	1.3 M	Flowing Oil:	100 C
Needle:	22 ga (f)	Injection Rate:	0.2 mL/min	Aging Time:	---

Wash: ---

Product Result: Needles clogged early in run; scrapped

Notes: Last experiment attempted with reused and washed syringes, new ones for each experiment from here on out

Experiment 33

HMTA / Urea:	1.64 M	Cerium Nitrate:	1.46 M	Flowing Oil:	100 C
Needle:	22 ga (f)	Injection Rate:	0.2 mL/min	Aging Time:	Undocumented

Wash: Hexane

Product Result: Many white spheres connected by unformed gel;

Notes: First two attempts gelled as soon as loaded into syringe; realized broth was not freezing as had thought earlier since second attempt was not chilled

Experiment 34

HMTA / Urea:	1.52 M	Cerium Nitrate:	1.58 M	Flowing Oil:	100 C
Needle:	18 ga (f)	Injection Rate:	0.3 mL/min	Aging Time:	30 min

Wash: Undocumented

Product Result: Many spheres with unformed gel

Notes: Broth was chilled in a freezer for over an hour rather than using ice bath

Experiment 35

HMTA / Urea:	2.06	Cerium Nitrate:	1.07	Flowing Oil:	100 C
Needle:	18 ga (f)	Injection Rate:	0.3 mL/min	Aging Time:	30 min

Wash: Undocumented

Product Result: After aging, some unformed gel, some white spheres, and some dark that are already cracked

Notes: This concentration was an accident, meant to be much lower; already knew this was too high

Experiment 36

HMTA / Urea:	1.42 M	Cerium Nitrate:	1.67 M	Flowing Oil:	100 C
Needle:	18 ga (f)	Injection Rate:	0.3 mL/min	Aging Time:	30 min

Wash: Hexane and 0.1 M Ammonium Hydroxide

Product Result: Some spheres and lots of unformed gel after aging; nearly all product dissolved or "melted" after washing

Notes: New smaller baskets made from 80 x 80 mesh

Experiment 37

HMTA / Urea:	1.66 M	Cerium Nitrate:	1.44 M	Flowing Oil:	100 C
Needle:	18 ga (f)	Injection Rate:	0.3 mL/min	Aging Time:	30 min

Wash: Hexane and 0.1 M Ammonium Hydroxide

Product Result: Large light colored and small darker spheres after aging; washed product placed in oven to dry

Notes: Small variations of injection rate show it needs to be between 0.1 and 0.2 mL/min

Experiment 38

HMTA / Urea:	1.65 M	Cerium Nitrate:	1.46 M	Flowing Oil:	100 C
Needle:	18 ga (f)	Injection Rate:	0.15mL/min	Aging Time:	30 min

Wash: Hexane and 0.1 M Ammonium Hydroxide

Product Result: Many spheres with very little unformed gel; majority of product melted when washed in Ammonium Hydroxide

Notes: This injection rate allowed a slow stream of uniform sized spheres to be produced

Experiment 39

HMTA / Urea:	1.65 M	Cerium Nitrate:	1.45 M	Flowing Oil:	100 C
Needle:	18 ga (f)	Injection Rate:	0.15 mL/min	Aging Time:	30 min

Wash: Hexane

Product Result: Many spheres with little if any unformed gel; after drying appear solid with no cracking

Notes: Spheres were placed in warm oven to dry

Experiment	40				
HMTA / Urea:	1.65 M	Cerium Nitrate:	1.46 M	Flowing Oil:	100 C
Needle:	18 ga (f)	Injection Rate:	0.15 mL/min	Aging Time:	30 min
Wash:	Hexane				
Product Result:	Not as well formed as #39; possibly caused by switching of needles in run				
Notes:	First needle clogged almost immediately				

Experiment	41				
HMTA / Urea:	1.67 M	Cerium Nitrate:	1.44 M	Flowing Oil:	100 C
Needle:	18 ga (f)	Injection Rate:	0.15 mL/min	Aging Time:	30 min
Wash:	Hexane				
Product Result:	Appear about the same as #39				
Notes:	Slightly higher HMTA and urea than #39, but similar results				

Experiment	42				
HMTA / Urea:	1.65 M	Cerium Nitrate:	1.45 M	Flowing Oil:	100 C
Needle:	18 ga (f)	Injection Rate:	0.15 mL/min	Aging Time:	30 min
Wash:	Hexane and 3 M Ammonium Hydroxide				
Product Result:	Spheres do not dissolve in Ammonium Hydroxide wash performed in a beaker; dried product appears chalky				
Notes:	First needle clogged right away then entire syringe began to gel				

Experiment	43				
HMTA / Urea:	1.65 M	Cerium Nitrate:	1.45 M	Flowing Oil:	100 C
Needle:	18 ga	Injection Rate:	0.15 mL/min	Aging Time:	30 min
Wash:	Hexane				
Product Result:	Appeared well formed after aging and still did after drying				
Notes:	Needle no longer placed in freezer after several clogged needles in previous runs				

Experiment	44				
HMTA / Urea:	1.65 M	Cerium Nitrate:	1.45 M	Flowing Oil:	100 C
Needle:	18 ga	Injection Rate:	0.15 mL/min	Aging Time:	30 min
Wash:	Hexane for all, and portion in two >40 minute washes of 3 M Ammonium Hydroxide				
Product Result:	Those undergoing second washing appear chalky and are crumbling				
Notes:	No longer experiencing early gelling since not freezing needles				

Experiment	45				
HMTA / Urea:	1.65 M	Cerium Nitrate:	1.46 M	Flowing Oil:	100 C
Needle:	18 ga (f)	Injection Rate:	0.15 mL/min	Aging Time:	30 min
Wash:	Hexane				
Product Result:	No defined areas of spheres; very sticky				
Notes:	Broth kept in freezer overnight; gelation is occurring near bottom of column				

Experiment 46

HMTA / Urea:	1.65 M	Cerium Nitrate:	1.45 M	Flowing Oil:	100 C
Needle:	18 ga	Injection Rate:	0.15 mL/min	Aging Time:	30 min

Wash: Hexane then half in two washes of 3 M Ammonium Hydroxide and Water

Product Result: Portion from second wash is dried, cracked, and crumbling

Notes: Have realized that this broth composition gives good quality spheres

Experiment 47

HMTA / Urea:	1.65 M	Cerium Nitrate:	1.45 M	Flowing Oil:	100 C
Needle:	18 ga	Injection Rate:	0.15 mL/min	Aging Time:	30 min

Wash: Hexane then half in 2 M Ammonium Hydroxide and rest in 1 M for 40 minutes then rinsed with Water

Product Result: All appear dry and cracked after dried

Notes: Trying to find the right concentration of Ammonium Hydroxide to wash in

Experiment 48

HMTA / Urea:	1.65 M	Cerium Nitrate:	1.45 M	Flowing Oil:	100 C
Needle:	18 ga	Injection Rate:	0.15 mL/min	Aging Time:	30 min

Wash: Hexane for all then half in 0.75 M Ammonium Hydroxide and rest in 0.5 M for under 40 minutes

Product Result: After drying product appears as a "goo"

Notes: Continued effort to find optimum wash solution

Experiment	49				
HMTA / Urea:	1.68 M	Cerium Nitrate:	1.43 M	Flowing Oil:	100 C
Needle:	18 ga	Injection Rate:	0.15 mL/min	Aging Time:	30 min
Wash:	Hexane, two 40 minute washes of 3 M Ammonium Hydroxide, then Water wash				
Product Result:	Most appear crumbling; some appear off white and still solid				
Notes:	Baskets now using 40 x 40 mesh on the bottom, allows washing in basket				

Experiment	50				
HMTA / Urea:	1.75 M	Cerium Nitrate:	1.36 M	Flowing Oil:	100 C
Needle:	18 ga	Injection Rate:	0.15 mL/min	Aging Time:	30 min
Wash:	Hexane then Oak Ridge Wash System				
Product Result:	Dried product appears cracked and crumbling				
Notes:	Discovery of Oak Ridge Wash in literature				

Experiment	51				
HMTA / Urea:	1.81 M	Cerium Nitrate:	1.3 M	Flowing Oil:	100 C
Needle:	18 ga	Injection Rate:	0.15 mL/min	Aging Time:	30 min
Wash:	Hexane then Oak Ridge Wash System				
Product Result:	More darker spheres produced as HMTA and Urea increased; product appears to be dissolving during wash; final dried product is cracked and crumbling				
Notes:	Increased amount of HMTA and urea				

Experiment	52				
HMTA / Urea:	1.68 M	Cerium Nitrate:	1.3 M	Flowing Oil:	100 C
Needle:	18 ga	Injection Rate:	0.15 mL/min	Aging Time:	30 min
Wash:	Hexane and Oak Ridge Wash for 60 minutes each step				
Product Result:	After washing placed in 50 C oven overnight; dried product is cracked and hollow				
Notes:	Attempt at broth composition that is used for uranium				

Experiment	53				
HMTA / Urea:	1.68 M	Cerium Nitrate:	1.43 M	Flowing Oil:	100 C
Needle:	18 ga	Injection Rate:	0.15 mL/min	Aging Time:	30 min
Wash:	Hexane then Oak Ridge Wash for 60 minutes each stage				
Product Result:	Placed in 40 C oven overnight; dried product is cracked and hollow				
Notes:	Increase amount of cerium nitrate to reduce amount of cracked and dried spheres				

Experiment	54				
HMTA / Urea:	1.65 M	Cerium Nitrate:	1.45 M	Flowing Oil:	100 C
Needle:	18 ga	Injection Rate:	0.15 mL/min	Aging Time:	30 min
Wash:	Hexane then Oak Ridge Wash for 60 minutes each stage				
Product Result:	Placed in 40 C over overnight; dried product is cracked and hollow				
Notes:	First attempt with broth composition that produced best spheres when only washed in hexane				

Experiment 55

HMTA / Urea:	1.65 M	Cerium Nitrate:	1.45 M	Flowing Oil:	100 C
Needle:	18 ga	Injection Rate:	0.15 mL/min	Aging Time:	60 min

Wash: Hexane then Oak Ridge Wash for 60 minutes each stage

Product Result: Washed product placed in front of fan to dry; some dried product appears brittle, under scope appears solid though

Notes: To dry faster, begin placing the washed spheres in front of a fan to dry

Experiment 56

HMTA / Urea:	1.65 M	Cerium Nitrate:	1.45 M	Flowing Oil:	100 C
Needle:	18 ga	Injection Rate:	0.15 mL/min	Aging Time:	90 min

Wash: Hexane then first stage of Oak Ridge Wash and a Water rinse; basket failed in middle

Product Result: Placed product in front of fan to dry; dried product is hollow and cracked

Notes: Increasing aging time while keeping other factors constant

Experiment 57

HMTA / Urea:	1.65 M	Cerium Nitrate:	1.45 M	Flowing Oil:	100 C
Needle:	18 ga	Injection Rate:	0.15 mL/min	Aging Time:	60 min

Wash: Oak Ridge Wash for 60 minutes each stage

Product Result: Placed in front of fan for 15 minutes to dry; dried product is cracked

Notes: No hexane wash in effort to produce quality washed spheres

Experiment 58

HMTA / Urea:	1.65 M	Cerium Nitrate:	1.45 M	Flowing Oil:	100 C
Needle:	18 ga	Injection Rate:	0.15 mL/min	Aging Time:	0 min

Wash: Hexane for 10 minutes then Oak Ridge Wash for 60 minutes each stage

Product Result: Placed in front of fan to dry, looked good when left; dried product has some very dark cracked spheres and some lighter ones

Notes: No aging done in effort to produce quality washed spheres

Experiment 59

HMTA / Urea:	1.65 M	Cerium Nitrate:	1.45 M	Flowing Oil:	90 C
Needle:	18 ga	Injection Rate:	0.15 mL/min	Aging Time:	60 min

Wash: Hexane then first stage of Oak Ridge Wash for 60 minutes and Water rinse

Product Result: Upon removal from oil had some unformed gel which dissolved during wash; dried product looks chalky but solid

Notes: Dropped temperature by 10 C; gelation occurred near bottom of column

Experiment 60

HMTA / Urea:	1.48 M	Cerium Nitrate:	1.29 M	Flowing Oil:	100 C
Needle:	18 ga	Injection Rate:	0.15 mL/min	Aging Time:	30 min

Wash: Hexane for 10 minutes ten Oak Ridge Wash for 60 minutes each stage

Product Result: Placed in front of fan to dry, look good upon leaving; dried product is dark and "crusty"; some appear good though

Notes: Diluting solutions by adding water; thought broth may have been too strong

Experiment	61				
HMTA / Urea:	1.42 M	Cerium Nitrate:	1.25 M	Flowing Oil:	100 C
Needle:	18 ga	Injection Rate:	0.15 mL/min	Aging Time:	60 min
Wash:	Hexane then Oak Ridge Wash for 60 minutes each stage				
Product Result:	Spheres and unformed gel formed, with unformed gel dissolving during washing				
Notes:	Further dilution of the broth by addition of water				

Experiment	62				
HMTA / Urea:	1.56 M	Cerium Nitrate:	1.37 M	Flowing Oil:	100 C
Needle:	18 ga	Injection Rate:	0.15 mL/min	Aging Time:	30 min
Wash:	Hexane then Oak Ridge Wash for 60 minutes each stage				
Product Result:	Dried product is a yellowish power with a few solid spheres				
Notes:	Used magnetic stirrer for washing; finding way to suspend basket over the spinning stirrer is an ordeal				

Experiment	63				
HMTA / Urea:	1.35 M	Cerium Nitrate:	1.05 M	Flowing Oil:	100 C
Needle:	18 ga	Injection Rate:	0.15 mL/min	Aging Time:	30 min
Wash:	Hexane then first stage of Oak Ridge Wash for 60 minutes				
Product Result:	Out of oil is few spheres and majority unformed gel; unformed gel dissolved in washing leaving just a sludge product				
Notes:	Too much water added in dilution process; gelation near bottom of column				

Experiment 64

HMTA / Urea:	1.65 M	Cerium Nitrate:	1.29 M	Flowing Oil:	100 C
Needle:	18 ga	Injection Rate:	0.15 mL/min	Aging Time:	30 min

Wash: Hexane wash for 10 minutes then Oak Ridge Wash for 75 minutes each stage

Product Result: Dried product is very crumbly

Notes: Basket fell on top of stirrer and bottom was torn off; length of wash increased because of this issue

Experiment 65

HMTA / Urea:	1.64 M	Cerium Nitrate:	1.46 M	Flowing Oil:	100 C
Needle:	18 ga	Injection Rate:	0.15 mL/min	Aging Time:	60 min

Wash: Hexane then Oak Ridge Wash for 60 minutes each stage

Product Result: Out of oil has some spheres and some unformed gel; most spheres look oblong and nonspherical; dried product is cracked and crumbling

Notes: Took amount of HMTA and urea below level typically used

Experiment 66

HMTA / Urea:	1.62 M	Cerium Nitrate:	1.42 M	Flowing Oil:	100 C
Needle:	18 ga	Injection Rate:	0.15 mL/min	Aging Time:	30 min

Wash: Hexane then Oak Ridge Wash for 60 minutes each stage

Product Result: Quite a bit of unformed gel when removed from oil; unformed product dissolves in wash; dried product is cracked and crumbling

Notes: Last attempt at diluting solution

Experiment 67

HMTA / Urea:	1.65 M	Cerium Nitrate:	1.45 M	Flowing Oil:	100 C
Needle:	18 ga	Injection Rate:	0.15 mL/min	Aging Time:	30 min

Wash: Hexane wash for 10 minutes then Oak Ridge Wash for 60 minutes each stage

Product Result: No unformed gel when removed from oil; lot of product dissolves in washing process; dried product is cracking; some solid spheres, but they are soft

Notes: Another attempt at this concentration with 30 minutes of aging

Experiment 68

HMTA / Urea:	1.65 M	Cerium Nitrate:	1.45 M	Flowing Oil:	100 C
Needle:	18 ga	Injection Rate:	0.15 mL/min	Aging Time:	70 min

Wash: Hexane, Water rinse, then Oak Ridge Wash for 75 minutes each stage, Water rinse

Product Result: Placed in front of fan to dry; dried product is cracked and crumbling

Notes: Same as #67 with increased aging and longer wash times

Experiment 69

HMTA / Urea:	1.65 M	Cerium Nitrate:	1.45 M	Flowing Oil:	110 C
Needle:	18 ga	Injection Rate:	0.15 mL/min	Aging Time:	60 min

Wash: Hexane wash for 15 minutes then Oak Ridge Wash for 75 minutes each stage

Product Result: Dried product is white and very powder like

Notes: Begin to increase oil temperature to speed the gelation process

Experiment	70				
HMTA / Urea:	1.65 M	Cerium Nitrate:	1.45 M	Flowing Oil:	115 C
Needle:	18 ga	Injection Rate:	0.15 mL/min	Aging Time:	60 min
Wash:	Hexane wash for 15 minutes then Oak Ridge Wash for 75 minutes each stage				
Product Result:	Dried product looks a lot like #69, very white and powder like				
Notes:	Further increase of the oil temperature				

APPENDIX B

DATA FROM SERIES OF SMALL SCALE INTERNAL GELATION TESTS

Volume 3.2 M HMTA/Urea (mL)	Vol. 3.0 M Cerium Nitrate (mL)	(Vol. HMTA and Urea) / (Vol. Cerium Nitrate)	Time to gelation per mL solution (s/mL)	Arbitrary Hardness
1	1	1	29	3
1	1	1	31	3
1	1	1	31.5	3.5
1.05	1	1.05	29.8	1.5
1.1	1	1.1	30.5	5
1.1	1	1.1	29.5	5
1.15	1	1.15	28.8	5
1.2	1	1.2	27.7	5
1.2	1	1.2	28.2	5
1.25	1	1.25	27.1	5
1.3	1	1.3	24.8	6
1.3	1	1.3	27.8	5
1.35	1	1.35	24.3	5.5
1.4	1	1.4	20.4	6

Volume 3.2 M HMTA/Urea (mL)	Vol. 3.0 M Cerium Nitrate (mL)	(Vol. HMTA and Urea) / (Vol. Cerium Nitrate)	Time to gelation per mL solution (s/mL)	Arbitrary Hardness
1.4	1	1.4	24.2	5.5
1.4	1	1.4	22.1	6
1.45	1	1.45	24.9	5.5
1.5	1	1.5	20.4	6.5
1.5	1	1.5	19.6	6
1.5	1	1.5	22.4	5
1.55	1.3	1.2	22.5	4.5
1.6	1	1.6	25.4	4.5
1.65	1	1.65	23.0	4.5
1.7	1	1.7	22.2	4.5
1.75	1	1.75	21.5	5
1.8	1	1.8	16.4	6
1.8	1	1.8	19.3	5
1.85	1	1.85	19.3	5.5
1.85	1	1.85	16.8	6
1.9	1	1.9	15.5	6
1.9	1	1.9	18.6	5.5

Volume 3.2 M HMTA/Urea (mL)	Vol. 3.0 M Cerium Nitrate (mL)	(Vol. HMTA and Urea) / (Vol. Cerium Nitrate)	Time to gelation per mL solution (s/mL)	Arbitrary Hardness
1.94	1	1.95	16.6	6
1.95	1	1.95	13.6	7
1.95	1.1	1.77	13.77	2
2	1	2	15.3	6
2	1	2	14.3	6
2.05	1	2.05	14.4	6
2.1	1.35	1.56	16.5	---

VITA

Name: Jeffrey John Wegener

Address: Department of Nuclear Engineering, Texas A&M University, 3133
TAMU College Station, TX 77843-3133

Email Address: wegenerj@tamu.edu

Education: B.S., Nuclear Engineering, Purdue University, 2004
M.S., Nuclear Engineering, Texas A&M University, 2008